CHAPTER 2

ATOMIC STRUCTURE AND INTERATOMIC BONDING

PROBLEM SOLUTIONS

Fundamental Concepts

Electrons in Atoms

2.1 *Cite the difference between atomic mass and atomic weight.*

Solution

Atomic mass is the mass of an individual atom, whereas atomic weight is the average (weighted) of the atomic masses of an atom's naturally occurring isotopes.

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2.2 *Chromium has four naturally-occurring isotopes: 4.34% of ^{50}Cr, with an atomic weight of 49.9460 amu, 83.79% of ^{52}Cr, with an atomic weight of 51.9405 amu, 9.50% of ^{53}Cr, with an atomic weight of 52.9407 amu, and 2.37% of ^{54}Cr, with an atomic weight of 53.9389 amu. On the basis of these data, confirm that the average atomic weight of Cr is 51.9963 amu.*

Solution

The average atomic weight of silicon ($\overline{A}_{Cr}$) is computed by adding fraction-of-occurrence/atomic weight products for the three isotopes. Thus

$$\overline{A}_{Cr} = f_{^{50}Cr} A_{^{50}Cr} + f_{^{52}Cr} A_{^{52}Cr} + f_{^{53}Cr} A_{^{53}Cr} + f_{^{54}Cr} A_{^{54}Cr}$$

$$= (0.0434)(49.9460 \text{ amu}) + (0.8379)(51.9405 \text{ amu}) + (0.0950)(52.9407 \text{ amu}) + (0.0237)(53.9389 \text{ amu}) = 51.9963 \text{ amu}$$

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2.3 *(a) How many grams are there in one amu of a material?*

(b) Mole, in the context of this book, is taken in units of gram-mole. On this basis, how many atoms are there in a pound-mole of a substance?

Solution

(a) In order to determine the number of grams in one amu of material, appropriate manipulation of the amu/atom, g/mol, and atom/mol relationships is all that is necessary, as

$$\#\,\text{g/amu} = \left(\frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{atoms}}\right)\left(\frac{1\ \text{g/mol}}{1\ \text{amu/atom}}\right)$$

$$= 1.66 \times 10^{-24}\ \text{g/amu}$$

(b) Since there are 453.6 g/lb_m,

$$1\ \text{lb-mol} = (453.6\ \text{g/lb}_\text{m})(6.022 \times 10^{23}\ \text{atoms/g-mol})$$

$$= 2.73 \times 10^{26}\ \text{atoms/lb-mol}$$

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2.4 *(a) Cite two important quantum-mechanical concepts associated with the Bohr model of the atom.*

(b) Cite two important additional refinements that resulted from the wave-mechanical atomic model.

Solution

(a) Two important quantum-mechanical concepts associated with the Bohr model of the atom are (1) that electrons are particles moving in discrete orbitals, and (2) electron energy is quantized into shells.

(b) Two important refinements resulting from the wave-mechanical atomic model are (1) that electron position is described in terms of a probability distribution, and (2) electron energy is quantized into both shells and subshells--each electron is characterized by four quantum numbers.

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2.5 *Relative to electrons and electron states, what does each of the four quantum numbers specify?*

Solution

The n quantum number designates the electron shell.

The l quantum number designates the electron subshell.

The m_l quantum number designates the number of electron states in each electron subshell.

The m_s quantum number designates the spin moment on each electron.

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2.6 *Allowed values for the quantum numbers of electrons are as follows:*

$$n = 1, 2, 3, \ldots$$

$$l = 0, 1, 2, 3, \ldots, n-1$$

$$m_l = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm l$$

$$m_s = \pm \frac{1}{2}$$

The relationships between n and the shell designations are noted in Table 2.1. Relative to the subshells,

$$l = 0 \text{ corresponds to an s subshell}$$

$$l = 1 \text{ corresponds to a p subshell}$$

$$l = 2 \text{ corresponds to a d subshell}$$

$$l = 3 \text{ corresponds to an f subshell}$$

For the K shell, the four quantum numbers for each of the two electrons in the 1s state, in the order of nlm_lm_s, are $100(\frac{1}{2})$ and $100(-\frac{1}{2})$. Write the four quantum numbers for all of the electrons in the L and M shells, and note which correspond to the s, p, and d subshells.

Solution

For the *L* state, $n = 2$, and eight electron states are possible. Possible l values are 0 and 1, while possible m_l values are 0 and ±1; and possible m_s values are $\pm\frac{1}{2}$. Therefore, for the *s* states, the quantum numbers are $200(\frac{1}{2})$ and $200(-\frac{1}{2})$. For the *p* states, the quantum numbers are $210(\frac{1}{2})$, $210(-\frac{1}{2})$, $211(\frac{1}{2})$, $211(-\frac{1}{2})$, $21(-1)(\frac{1}{2})$, and $21(-1)(-\frac{1}{2})$.

For the *M* state, $n = 3$, and 18 states are possible. Possible l values are 0, 1, and 2; possible m_l values are 0, ±1, and ±2; and possible m_s values are $\pm\frac{1}{2}$. Therefore, for the *s* states, the quantum numbers are $300(\frac{1}{2})$, $300(-\frac{1}{2})$, for the *p* states they are $310(\frac{1}{2})$, $310(-\frac{1}{2})$, $311(\frac{1}{2})$, $311(-\frac{1}{2})$, $31(-1)(\frac{1}{2})$, and $31(-1)(-\frac{1}{2})$; for the *d* states they are $320(\frac{1}{2})$, $320(-\frac{1}{2})$, $321(\frac{1}{2})$, $321(-\frac{1}{2})$, $32(-1)(\frac{1}{2})$, $32(-1)(-\frac{1}{2})$, $322(\frac{1}{2})$, $322(-\frac{1}{2})$, $32(-2)(\frac{1}{2})$, and $32(-2)(-\frac{1}{2})$.

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2.7 *Give the electron configurations for the following ions: Fe^{2+}, Al^{3+}, Cu^{+}, Ba^{2+}, Br^{-}, and O^{2-}.*

Solution

The electron configurations for the ions are determined using Table 2.2 (and Figure 2.6).

Fe^{2+}: From Table 2.2, the electron configuration for an atom of iron is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$. In order to become an ion with a plus two charge, it must lose two electrons—in this case the two 4*s*. Thus, the electron configuration for an Fe^{2+} ion is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.

Al^{3+}: From Table 2.2, the electron configuration for an atom of aluminum is $1s^2 2s^2 2p^6 3s^2 3p^1$. In order to become an ion with a plus three charge, it must lose three electrons—in this case two 3*s* and the one 3*p*. Thus, the electron configuration for an Al^{3+} ion is $1s^2 2s^2 2p^6$.

Cu^{+}: From Table 2.2, the electron configuration for an atom of copper is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$. In order to become an ion with a plus one charge, it must lose one electron—in this case the 4*s*. Thus, the electron configuration for a Cu^{+} ion is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$.

Ba^{2+}: The atomic number for barium is 56 (Figure 2.6), and inasmuch as it is not a transition element the electron configuration for one of its atoms is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$. In order to become an ion with a plus two charge, it must lose two electrons—in this case two the 6*s*. Thus, the electron configuration for a Ba^{2+} ion is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$.

Br^{-}: From Table 2.2, the electron configuration for an atom of bromine is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$. In order to become an ion with a minus one charge, it must acquire one electron—in this case another 4*p*. Thus, the electron configuration for a Br^{-} ion is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$.

O^{2-}: From Table 2.2, the electron configuration for an atom of oxygen is $1s^2 2s^2 2p^4$. In order to become an ion with a minus two charge, it must acquire two electrons—in this case another two 2*p*. Thus, the electron configuration for an O^{2-} ion is $1s^2 2s^2 2p^6$.

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2.8 *Sodium chloride (NaCl) exhibits predominantly ionic bonding. The Na^+ and Cl^- ions have electron structures that are identical to which two inert gases?*

Solution

The Na^+ ion is just a sodium atom that has lost one electron; therefore, it has an electron configuration the same as neon (Figure 2.6).

The Cl^- ion is a chlorine atom that has acquired one extra electron; therefore, it has an electron configuration the same as argon.

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The Periodic Table

2.9 *With regard to electron configuration, what do all the elements in Group VIIA of the periodic table have in common?*

Solution

Each of the elements in Group VIIA has five *p* electrons.

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2.10 *To what group in the periodic table would an element with atomic number 114 belong?*

Solution

From the periodic table (Figure 2.6) the element having atomic number 114 would belong to group IVA. According to Figure 2.6, Ds, having an atomic number of 110 lies below Pt in the periodic table and in the right-most column of group VIII. Moving four columns to the right puts element 114 under Pb and in group IVA.

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2.11 *Without consulting Figure 2.6 or Table 2.2, determine whether each of the electron configurations given below is an inert gas, a halogen, an alkali metal, an alkaline earth metal, or a transition metal. Justify your choices.*

(a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$

(b) $1s^2 2s^2 2p^6 3s^2 3p^6$

(c) $1s^2 2s^2 2p^5$

(d) $1s^2 2s^2 2p^6 3s^2$

(e) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$

(f) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

Solution

(a) The $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$ electron configuration is that of a transition metal because of an incomplete *d* subshell.

(b) The $1s^2 2s^2 2p^6 3s^2 3p^6$ electron configuration is that of an inert gas because of filled 3*s* and 3*p* subshells.

(c) The $1s^2 2s^2 2p^5$ electron configuration is that of a halogen because it is one electron deficient from having a filled *L* shell.

(d) The $1s^2 2s^2 2p^6 3s^2$ electron configuration is that of an alkaline earth metal because of two *s* electrons.

(e) The $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$ electron configuration is that of a transition metal because of an incomplete *d* subshell.

(f) The $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ electron configuration is that of an alkali metal because of a single *s* electron.

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2.12 *(a) What electron subshell is being filled for the rare earth series of elements on the periodic table?*

(b) What electron subshell is being filled for the actinide series?

Solution

(a) The 4*f* subshell is being filled for the rare earth series of elements.

(b) The 5*f* subshell is being filled for the actinide series of elements.

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Bonding Forces and Energies

2.13 *Calculate the force of attraction between a K^+ and an O^{2-} ion the centers of which are separated by a distance of 1.5 nm.*

Solution

The attractive force between two ions F_A is just the derivative with respect to the interatomic separation of the attractive energy expression, Equation 2.8, which is just

$$F_A = \frac{dE_A}{dr} = \frac{d\left(-\frac{A}{r}\right)}{dr} = \frac{A}{r^2}$$

The constant A in this expression is defined in footnote 3. Since the valences of the K^+ and O^{2-} ions (Z_1 and Z_2) are +1 and -2, respectively, $Z_1 = 1$ and $Z_2 = 2$, then

$$F_A = \frac{(Z_1 e)(Z_2 e)}{4\pi\varepsilon_0 r^2}$$

$$= \frac{(1)(2)(1.602 \times 10^{-19}\ \text{C})^2}{(4)(\pi)(8.85 \times 10^{-12}\ \text{F/m})(1.5 \times 10^{-9}\ \text{m})^2}$$

$$= 2.05 \times 10^{-10}\ \text{N}$$

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2.14 *The net potential energy between two adjacent ions, E_N, may be represented by the sum of Equations 2.8 and 2.9; that is,*

$$E_N = -\frac{A}{r} + \frac{B}{r^n}$$

Calculate the bonding energy E_0 in terms of the parameters A, B, and n using the following procedure:

1. Differentiate E_N with respect to r, and then set the resulting expression equal to zero, since the curve of E_N versus r is a minimum at E_0.

2. Solve for r in terms of A, B, and n, which yields r_0, the equilibrium interionic spacing.

3. Determine the expression for E_0 by substitution of r_0 into Equation 2.11.

Solution

(a) Differentiation of Equation 2.11 yields

$$\frac{dE_N}{dr} = \frac{d\left(-\frac{A}{r}\right)}{dr} + \frac{d\left(\frac{B}{r^n}\right)}{dr}$$

$$= \frac{A}{r^{(1+1)}} - \frac{nB}{r^{(n+1)}} = 0$$

(b) Now, solving for r ($= r_0$)

$$\frac{A}{r_0^2} = \frac{nB}{r_0^{(n+1)}}$$

or

$$r_0 = \left(\frac{A}{nB}\right)^{1/(1-n)}$$

(c) Substitution for r_0 into Equation 2.11 and solving for E ($= E_0$)

$$E_0 = -\frac{A}{r_0} + \frac{B}{r_0^n}$$

$$= -\frac{A}{\left(\frac{A}{nB}\right)^{1/(1-n)}} + \frac{B}{\left(\frac{A}{nB}\right)^{n/(1-n)}}$$

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2.15 *For a K^+–Cl^- ion pair, attractive and repulsive energies E_A and E_R, respectively, depend on the distance between the ions r, according to*

$$E_A = -\frac{1.436}{r}$$

$$E_R = \frac{5.8 \times 10^{-6}}{r^9}$$

For these expressions, energies are expressed in electron volts per K^+–Cl^- pair, and r is the distance in nanometers. The net energy E_N is just the sum of the two expressions above.

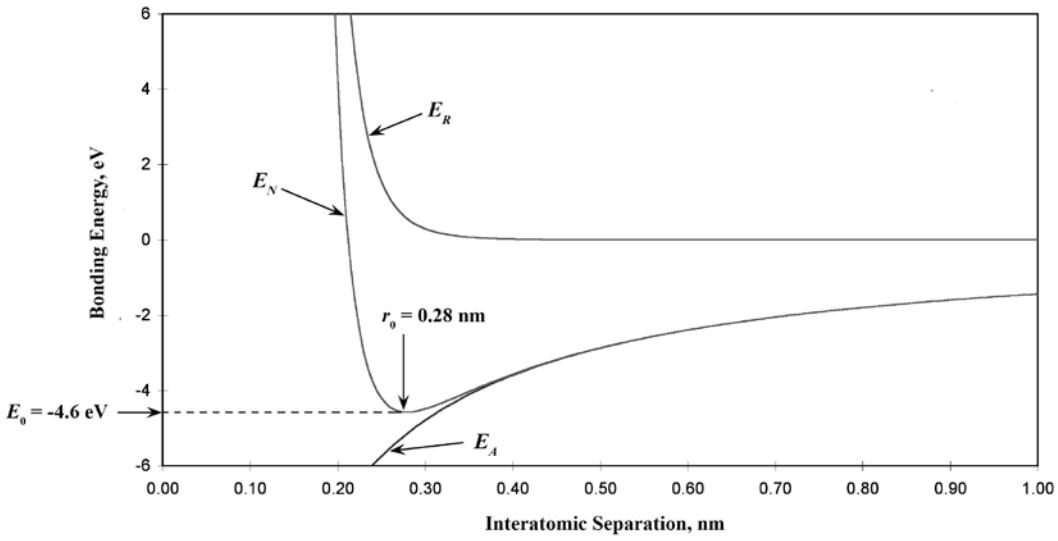
(a) Superimpose on a single plot E_N, E_R, and E_A versus r up to 1.0 nm.

(b) On the basis of this plot, determine (i) the equilibrium spacing r_0 between the K^+ and Cl^- ions, and (ii) the magnitude of the bonding energy E_0 between the two ions.

(c) Mathematically determine the r_0 and E_0 values using the solutions to Problem 2.14 and compare these with the graphical results from part (b).

Solution

(a) Curves of E_A, E_R, and E_N are shown on the plot below.



(b) From this plot

$r_0 = 0.28$ nm

$E_0 = -4.6$ eV

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(c) From Equation 2.11 for E_N

$$A = 1.436$$

$$B = 5.86 \times 10^{-6}$$

$$n = 9$$

Thus,

$$r_0 = \left(\frac{A}{nB}\right)^{1/(1\ -\ n)}$$

$$= \left[\frac{1.436}{(8)(5.86\ \times\ 10^{-6})}\right]^{1/(1\ -\ 9)} = 0.279\ \text{nm}$$

and

$$E_0 = -\frac{A}{\left(\frac{A}{nB}\right)^{1/(1\ -\ n)}} + \frac{B}{\left(\frac{A}{nB}\right)^{n/(1\ -\ n)}}$$

$$= -\frac{1.436}{\left[\frac{1.436}{(9)(5.86 \times 10^{-6})}\right]^{1/(1\ -\ 9)}} + \frac{5.86\ \times\ 10^{-6}}{\left[\frac{1.436}{(9)(5.86 \times 10^{-6})}\right]^{9/(1\ -\ 9)}}$$

$$= -4.57\ \text{eV}$$

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2.16 *Consider a hypothetical X^+-Y^- ion pair for which the equilibrium interionic spacing and bonding energy values are 0.35 nm and -6.13 eV, respectively. If it is known that n in Equation 2.11 has a value of 10, using the results of Problem 2.14, determine explicit expressions for attractive and repulsive energies E_A and E_R of Equations 2.8 and 2.9.*

Solution

This problem gives us, for a hypothetical X^+-Y^- ion pair, values for r_0 (0.35 nm), E_0 (– 6.13 eV), and n (10), and asks that we determine explicit expressions for attractive and repulsive energies of Equations 2.8 and 2.9. In essence, it is necessary to compute the values of A and B in these equations. Expressions for r_0 and E_0 in terms of n, A, and B were determined in Problem 2.14, which are as follows:

$$r_0 = \left(\frac{A}{nB}\right)^{1/(1\,-\,n)}$$

$$E_0 = -\frac{A}{\left(\frac{A}{nB}\right)^{1/(1\,-\,n)}} + \frac{B}{\left(\frac{A}{nB}\right)^{n/(1\,-\,n)}}$$

Thus, we have two simultaneous equations with two unknowns (viz. A and B). Upon substitution of values for r_0 and E_0 in terms of n, these equations take the forms

$$0.35\text{ nm} = \left(\frac{A}{10B}\right)^{1/(1\,-\,10)} = \left(\frac{A}{10B}\right)^{-1/9}$$

and

$$-6.13\text{ eV} = -\frac{A}{\left(\frac{A}{10B}\right)^{1/(1\,-\,10)}} + \frac{B}{\left(\frac{A}{10B}\right)^{10/(1\,-\,10)}}$$

$$= -\frac{A}{\left(\frac{A}{10B}\right)^{-1/9}} + \frac{B}{\left(\frac{A}{10B}\right)^{-10/9}}$$

We now want to solve these two equations simultaneously for values of A and B. From the first of these two equations, solving for $A/8B$ leads to

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$$\frac{A}{10B} = (0.35\ \text{nm})^{-9}$$

Furthermore, from the above equation the A is equal to

$$A = 10B(0.35\ \text{nm})^{-9}$$

When the above two expressions for $A/10B$ and A are substituted into the above expression for E_0 (- 6.13 eV), the following results

$$-6.13\ \text{eV} = = -\frac{A}{\left(\frac{A}{10B}\right)^{-1/9}} + \frac{B}{\left(\frac{A}{10B}\right)^{-10/9}}$$

$$= -\frac{10B(0.35\ \text{nm})^{-9}}{\left[(0.35\ \text{nm})^{-9}\right]^{-1/9}} + \frac{B}{\left[(0.35\ \text{nm})^{-9}\right]^{10/9}}$$

$$= -\frac{10B(0.35\ \text{nm})^{-9}}{0.35\ \text{nm}} + \frac{B}{(0.35\ \text{nm})^{10}}$$

Or

$$-6.13\ \text{eV} = = -\frac{10B}{(0.35\ \text{nm})^{10}} + \frac{B}{(0.35\ \text{nm})^{10}} = -\frac{9B}{(0.35\ \text{nm})^{10}}$$

Solving for B from this equation yields

$$B = 1.88 \times 10^{-5}\ \text{eV-nm}^{10}$$

Furthermore, the value of A is determined from one of the previous equations, as follows:

$$A = 10B(0.35\ \text{nm})^{-9} = (10)\left(1.88 \times 10^{-5}\ \text{eV-nm}^{10}\right)(0.35\ \text{nm})^{-9}$$

$$= 2.39\ \text{eV-nm}$$

Thus, Equations 2.8 and 2.9 become

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$$E_A = -\frac{2.39}{r}$$

$$E_R = \frac{1.88 \times 10^{-5}}{r^{10}}$$

Of course these expressions are valid for r and E in units of nanometers and electron volts, respectively.

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2.17 *The net potential energy E_N between two adjacent ions is sometimes represented by the expression*

$$E_N = -\frac{C}{r} + D\exp\left(-\frac{r}{\rho}\right) \tag{2.12}$$

in which r is the interionic separation and C, D, and ρ are constants whose values depend on the specific material.

(a) Derive an expression for the bonding energy E_0 in terms of the equilibrium interionic separation r_0 and the constants D and ρ using the following procedure:

1. Differentiate E_N with respect to r and set the resulting expression equal to zero.

2. Solve for C in terms of D, ρ, and r_0.

3. Determine the expression for E_0 by substitution for C in Equation 2.12.

(b) Derive another expression for E_0 in terms of r_0, C, and ρ using a procedure analogous to the one outlined in part (a).

Solution

(a) Differentiating Equation 2.12 with respect to *r* yields

$$\frac{dE}{dr} = \frac{d\left(-\frac{C}{r}\right)}{dr} - \frac{d\left[D\exp\left(-\frac{r}{\rho}\right)\right]}{dr}$$

$$= \frac{C}{r^2} - \frac{De^{-r/\rho}}{\rho}$$

At $r = r_0$, $dE/dr = 0$, and

$$\frac{C}{r_0^2} = \frac{De^{-(r_0/\rho)}}{\rho} \tag{2.12b}$$

Solving for *C* and substitution into Equation 2.12 yields an expression for E_0 as

$$E_0 = De^{-(r_0/\rho)}\left(1 - \frac{r_0}{\rho}\right)$$

(b) Now solving for *D* from Equation 2.12b above yields

$$D = \frac{C\rho\, e^{(r_0/\rho)}}{r_0^2}$$

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Substitution of this expression for D into Equation 2.12 yields an expression for E_0 as

$$E_0 = \frac{C}{r_0}\left(\frac{\rho}{r_0} - 1\right)$$

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Primary Interatomic Bonds

2.18 *(a) Briefly cite the main differences between ionic, covalent, and metallic bonding.*

(b) State the Pauli exclusion principle.

Solution

(a) The main differences between the various forms of primary bonding are:

Ionic--there is electrostatic attraction between oppositely charged ions.

Covalent--there is electron sharing between two adjacent atoms such that each atom assumes a stable electron configuration.

Metallic--the positively charged ion cores are shielded from one another, and also "glued" together by the sea of valence electrons.

(b) The Pauli exclusion principle states that each electron state can hold no more than two electrons, which must have opposite spins.

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2.19 *Compute the percents ionic character of the interatomic bonds for the following compounds: TiO_2, ZnTe, CsCl, InSb, and $MgCl_2$.*

Solution

The percent ionic character is a function of the electron negativities of the ions X_A and X_B according to Equation 2.10. The electronegativities of the elements are found in Figure 2.7.

For TiO_2, $X_{Ti} = 1.5$ and $X_O = 3.5$, and therefore,

$$\%IC = \left[1 - e^{(-0.25)(3.5-1.5)^2}\right] \times 100 = 63.2\%$$

For ZnTe, $X_{Zn} = 1.6$ and $X_{Te} = 2.1$, and therefore,

$$\%IC = \left[1 - e^{(-0.25)(2.1-1.6)^2}\right] \times 100 = 6.1\%$$

For CsCl, $X_{Cs} = 0.7$ and $X_{Cl} = 3.0$, and therefore,

$$\%IC = \left[1 - e^{(-0.25)(3.0-0.7)^2}\right] \times 100 = 73.4\%$$

For InSb, $X_{In} = 1.7$ and $X_{Sb} = 1.9$, and therefore,

$$\%IC = \left[1 - e^{(-0.25)(1.9-1.7)^2}\right] \times 100 = 1.0\%$$

For $MgCl_2$, $X_{Mg} = 1.2$ and $X_{Cl} = 3.0$, and therefore,

$$\%IC = \left[1 - e^{(-0.25)(3.0-1.2)^2}\right] \times 100 = 55.5\%$$

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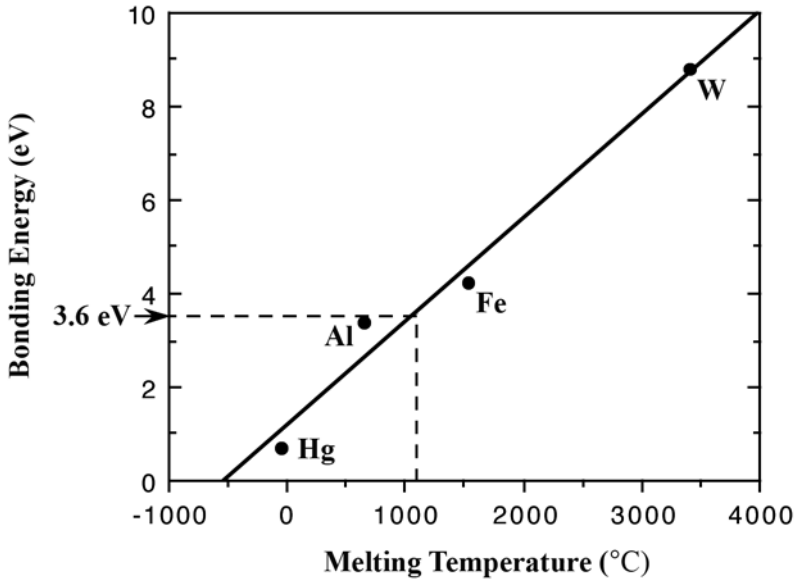
2.20 *Make a plot of bonding energy versus melting temperature for the metals listed in Table 2.3. Using this plot, approximate the bonding energy for copper, which has a melting temperature of 1084°C.*

Solution

Below is plotted the bonding energy versus melting temperature for these four metals. From this plot, the bonding energy for copper (melting temperature of 1084°C) should be approximately 3.6 eV. The experimental value is 3.5 eV.



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2.21 *Using Table 2.2, determine the number of covalent bonds that are possible for atoms of the following elements: germanium, phosphorus, selenium, and chlorine.*

Solution

For germanium, having the valence electron structure $4s^2 4p^2$, $N' = 4$; thus, there are $8 - N' = 4$ covalent bonds per atom.

For phosphorus, having the valence electron structure $3s^2 3p^3$, $N' = 5$; thus, there is $8 - N' = 3$ covalent bonds per atom.

For selenium, having the valence electron structure $4s^2 4p^4$, $N' = 6$; thus, there are $8 - N' = 2$ covalent bonds per atom.

For chlorine, having the valence electron structure $3s^2 3p^5$, $N' = 7$; thus, there are $8 - N' = 1$ covalent bond per atom.

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2.22 *What type(s) of bonding would be expected for each of the following materials: brass (a copper-zinc alloy), rubber, barium sulfide (BaS), solid xenon, bronze, nylon, and aluminum phosphide (AlP)?*

Solution

For brass, the bonding is metallic since it is a metal alloy.

For rubber, the bonding is covalent with some van der Waals. (Rubber is composed primarily of carbon and hydrogen atoms.)

For BaS, the bonding is predominantly ionic (but with some covalent character) on the basis of the relative positions of Ba and S in the periodic table.

For solid xenon, the bonding is van der Waals since xenon is an inert gas.

For bronze, the bonding is metallic since it is a metal alloy (composed of copper and tin).

For nylon, the bonding is covalent with perhaps some van der Waals. (Nylon is composed primarily of carbon and hydrogen.)

For AlP the bonding is predominantly covalent (but with some ionic character) on the basis of the relative positions of Al and P in the periodic table.

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Secondary Bonding or van der Waals Bonding

2.23 *Explain why hydrogen fluoride (HF) has a higher boiling temperature than hydrogen chloride (HCl) (19.4 vs. –85°C), even though HF has a lower molecular weight.*

Solution

The intermolecular bonding for HF is hydrogen, whereas for HCl, the intermolecular bonding is van der Waals. Since the hydrogen bond is stronger than van der Waals, HF will have a higher melting temperature.

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CHAPTER 3

THE STRUCTURE OF CRYSTALLINE SOLIDS

PROBLEM SOLUTIONS

Fundamental Concepts

3.1 *What is the difference between atomic structure and crystal structure?*

Solution

Atomic structure relates to the number of protons and neutrons in the nucleus of an atom, as well as the number and probability distributions of the constituent electrons. On the other hand, crystal structure pertains to the arrangement of atoms in the crystalline solid material.

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Unit Cells
Metallic Crystal Structures

3.2 *If the atomic radius of aluminum is 0.143 nm, calculate the volume of its unit cell in cubic meters.*

Solution

For this problem, we are asked to calculate the volume of a unit cell of aluminum. Aluminum has an FCC crystal structure (Table 3.1). The FCC unit cell volume may be computed from Equation 3.4 as

$$V_C = 16R^3\sqrt{2} = (16)\left(0.143 \times 10^{-9}\ \text{m}\right)^3\left(\sqrt{2}\right) = 6.62 \times 10^{-29}\ \text{m}^3$$

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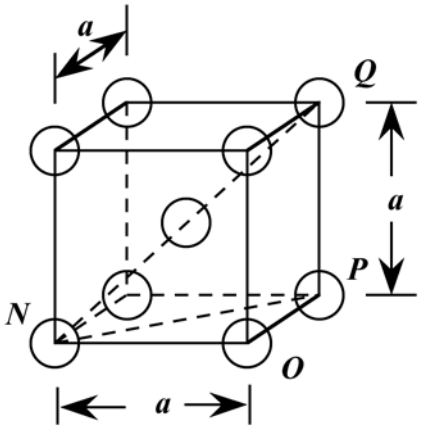
3.3 *Show for the body-centered cubic crystal structure that the unit cell edge length a and the atomic radius R are related through a =*$4R/\sqrt{3}$.

Solution

Consider the BCC unit cell shown below



Using the triangle *NOP*

$$(\overline{NP})^2 = a^2 + a^2 = 2a^2$$

And then for triangle *NPQ*,

$$(\overline{NQ})^2 = (\overline{QP})^2 + (\overline{NP})^2$$

But $\overline{NQ} = 4R$, *R* being the atomic radius. Also, $\overline{QP} = a$. Therefore,

$$(4R)^2 = a^2 + 2a^2$$

or

$$a = \frac{4R}{\sqrt{3}}$$

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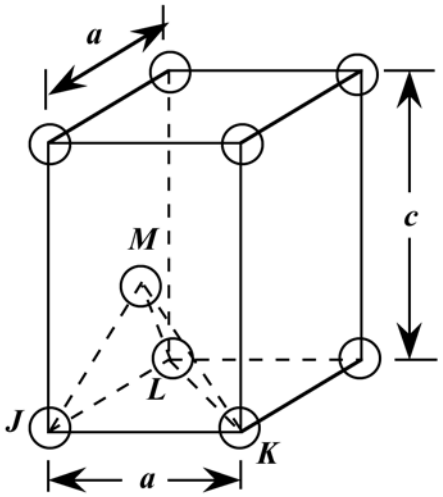
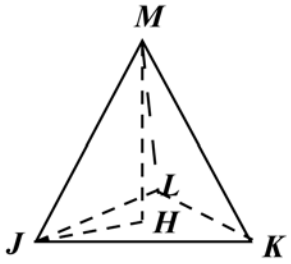
3.4 *For the HCP crystal structure, show that the ideal c/a ratio is 1.633.*

Solution

A sketch of one-third of an HCP unit cell is shown below.



Consider the tetrahedron labeled as *JKLM*, which is reconstructed as



The atom at point *M* is midway between the top and bottom faces of the unit cell--that is $\overline{MH} = c/2$. And, since atoms at points *J*, *K*, and *M*, all touch one another,

$$\overline{JM} = \overline{JK} = 2R = a$$

where *R* is the atomic radius. Furthermore, from triangle *JHM*,

$$(\overline{JM})^2 = (\overline{JH})^2 + (\overline{MH})^2$$

or

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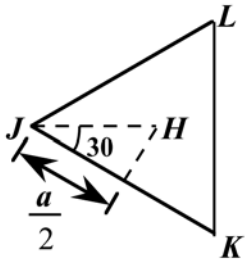
$$a^2 = (\overline{JH})^2 + \left(\frac{c}{2}\right)^2$$

Now, we can determine the $\overline{JH}$ length by consideration of triangle *JKL*, which is an equilateral triangle,



$$\cos 30° = \frac{a/2}{JH} = \frac{\sqrt{3}}{2}$$

and

$$\overline{JH} = \frac{a}{\sqrt{3}}$$

Substituting this value for $\overline{JH}$ in the above expression yields

$$a^2 = \left(\frac{a}{\sqrt{3}}\right)^2 + \left(\frac{c}{2}\right)^2 = \frac{a^2}{3} + \frac{c^2}{4}$$

and, solving for *c/a*

$$\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$$

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3.5 *Show that the atomic packing factor for BCC is 0.68.*

Solution

The atomic packing factor is defined as the ratio of sphere volume to the total unit cell volume, or

$$\text{APF} = \frac{V_S}{V_C}$$

Since there are two spheres associated with each unit cell for BCC

$$V_S = 2(\text{sphere volume}) = 2\left(\frac{4\pi R^3}{3}\right) = \frac{8\pi R^3}{3}$$

Also, the unit cell has cubic symmetry, that is $V_C = a^3$. But a depends on R according to Equation 3.3, and

$$V_C = \left(\frac{4R}{\sqrt{3}}\right)^3 = \frac{64R^3}{3\sqrt{3}}$$

Thus,

$$\text{APF} = \frac{V_S}{V_C} = \frac{8\pi R^3/3}{64R^3/3\sqrt{3}} = 0.68$$

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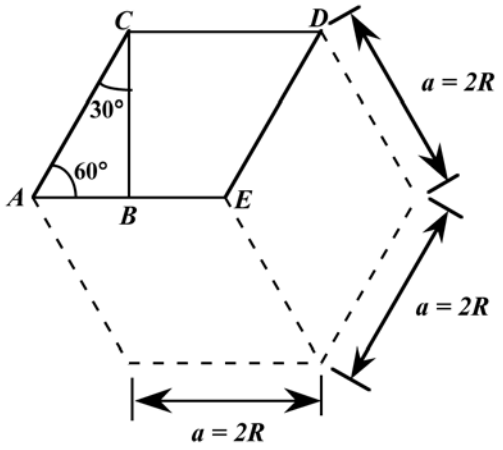
3.6 *Show that the atomic packing factor for HCP is 0.74.*

Solution

The APF is just the total sphere volume-unit cell volume ratio. For HCP, there are the equivalent of six spheres per unit cell, and thus

$$V_S = 6\left(\frac{4\pi R^3}{3}\right) = 8\pi R^3$$

Now, the unit cell volume is just the product of the base area times the cell height, c. This base area is just three times the area of the parallelepiped $ACDE$ shown below.



The area of $ACDE$ is just the length of $\overline{CD}$ times the height $\overline{BC}$. But $\overline{CD}$ is just a or $2R$, and

$$\overline{BC} = 2R\cos(30°) = \frac{2R\sqrt{3}}{2}$$

Thus, the base area is just

$$\text{AREA} = (3)(\overline{CD})(\overline{BC}) = (3)(2R)\left(\frac{2R\sqrt{3}}{2}\right) = 6R^2\sqrt{3}$$

and since $c = 1.633a = 2R(1.633)$

$$V_C = (\text{AREA})(c) = 6R^2c\sqrt{3} \qquad (3.S1)$$

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$$= \left(6R^2\sqrt{3}\right)(2)(1.633)R = 12\sqrt{3}\,(1.633)\,R^3$$

Thus,

$$\text{APF} = \frac{V_S}{V_C} = \frac{8\pi R^3}{12\sqrt{3}\,(1.633)\,R^3} = 0.74$$

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Density Computations

3.7 *Iron has a BCC crystal structure, an atomic radius of 0.124 nm, and an atomic weight of 55.85 g/mol. Compute and compare its theoretical density with the experimental value found inside the front cover.*

Solution

This problem calls for a computation of the density of iron. According to Equation 3.5

$$\rho = \frac{nA_{\text{Fe}}}{V_C N_{\text{A}}}$$

For BCC, n = 2 atoms/unit cell, and

$$V_C = \left(\frac{4R}{\sqrt{3}}\right)^3$$

Thus,

$$\rho = \frac{nA_{\text{Fe}}}{\left(\frac{4R}{\sqrt{3}}\right)^3 N_{\text{A}}}$$

$$= \frac{(2 \text{ atoms/unit cell})(55.85 \text{ g/mol})}{\left[(4)\left(0.124 \times 10^{-7} \text{ cm}\right)/\sqrt{3}\right]^3 /(\text{unit cell})\left(6.022 \times 10^{23} \text{ atoms/mol}\right)}$$

$$= 7.90 \text{ g/cm}^3$$

The value given inside the front cover is 7.87 g/cm^3.

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3.8 *Calculate the radius of an iridium atom, given that Ir has an FCC crystal structure, a density of 22.4 g/cm^3, and an atomic weight of 192.2 g/mol.*

Solution

We are asked to determine the radius of an iridium atom, given that Ir has an FCC crystal structure. For FCC, $n = 4$ atoms/unit cell, and $V_C = 16R^3\sqrt{2}$ (Equation 3.4). Now,

$$\rho = \frac{nA_{\text{Ir}}}{V_C N_{\text{A}}}$$

$$= \frac{nA_{\text{Ir}}}{(16R^3\sqrt{2})N_{\text{A}}}$$

And solving for R from the above expression yields

$$R = \left(\frac{nA_{\text{Ir}}}{16\rho N_{\text{A}}\sqrt{2}}\right)^{1/3}$$

$$= \left[\frac{(4 \text{ atoms/unit cell})(192.2 \text{ g/mol})}{(16)(22.4 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})(\sqrt{2})}\right]^{1/3}$$

$$= 1.36 \times 10^{-8} \text{ cm} = 0.136 \text{ nm}$$

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3.9 *Calculate the radius of a vanadium atom, given that V has a BCC crystal structure, a density of 5.96 g/cm^3, and an atomic weight of 50.9 g/mol.*

Solution

This problem asks for us to calculate the radius of a vanadium atom. For BCC, n = 2 atoms/unit cell, and

$$V_C = \left(\frac{4R}{\sqrt{3}}\right)^3 = \frac{64R^3}{3\sqrt{3}}$$

Since, from Equation 3.5

$$\rho = \frac{nA_V}{V_C N_A}$$

$$= \frac{nA_V}{\left(\frac{64R^3}{3\sqrt{3}}\right)N_A}$$

and solving for R the previous equation

$$R = \left(\frac{3\sqrt{3}nA_V}{64\rho N_A}\right)^{1/3}$$

and incorporating values of parameters given in the problem statement

$$R = \left[\frac{\left(3\sqrt{3}\right)(2 \text{ atoms/unit cell})(50.9 \text{ g/mol})}{(64)\left(5.96 \text{ g/cm}^3\right)\left(6.022 \times 10^{23} \text{ atoms/mol}\right)}\right]^{1/3}$$

$$= 1.32 \times 10^{-8} \text{ cm} = 0.132 \text{ nm}$$

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3.10 *Some hypothetical metal has the simple cubic crystal structure shown in Figure 3.24. If its atomic weight is 70.4 g/mol and the atomic radius is 0.126 nm, compute its density.*

Solution

For the simple cubic crystal structure, the value of n in Equation 3.5 is unity since there is only a single atom associated with each unit cell. Furthermore, for the unit cell edge length, $a = 2R$ (Figure 3.24). Therefore, employment of Equation 3.5 yields

$$\rho = \frac{nA}{V_C N_A} = \frac{nA}{(2R)^3 N_A}$$

and incorporating values of the other parameters provided in the problem statement leads to

$$\rho = \frac{(1 \text{ atom/unit cell})(70.4 \text{ g/mol})}{\left\{\left[(2)\left(1.26 \times 10^{-8} \text{ cm}\right)\right]^3/(\text{unit cell})\right\}\left(6.022 \times 10^{23} \text{ atoms/mol}\right)}$$

$$7.31 \text{ g/cm}^3$$

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3.11 *Zirconium has an HCP crystal structure and a density of 6.51 g/cm^3.*

(a) What is the volume of its unit cell in cubic meters?

(b) If the c/a ratio is 1.593, compute the values of c and a.

Solution

(a) The volume of the Zr unit cell may be computed using Equation 3.5 as

$$V_C = \frac{nA_{Zr}}{\rho N_A}$$

Now, for HCP, n = 6 atoms/unit cell, and for Zr, A_{Zr} = 91.22 g/mol. Thus,

$$V_C = \frac{(6 \text{ atoms/unit cell})(91.22 \text{ g/mol})}{(6.51 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 1.396 \times 10^{-22} \text{ cm}^3\text{/unit cell} = 1.396 \times 10^{-28} \text{ m}^3\text{/unit cell}$$

(b) From Equation 3.S1 of the solution to Problem 3.6, for HCP

$$V_C = 6R^2c\sqrt{3}$$

But, since $a = 2R$, (i.e., $R = a/2$) then

$$V_C = 6\left(\frac{a}{2}\right)^2 c\sqrt{3} = \frac{3\sqrt{3}\,a^2c}{2}$$

but, since $c = 1.593a$

$$V_C = \frac{3\sqrt{3}\,(1.593)\,a^3}{2} = 1.396 \times 10^{-22} \text{ cm}^3\text{/unit cell}$$

Now, solving for a

$$a = \left[\frac{(2)(1.396 \times 10^{-22} \text{ cm}^3)}{(3)(\sqrt{3})(1.593)}\right]^{1/3}$$

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$$= 3.23 \times 10^{-8} \text{ cm} = 0.323 \text{ nm}$$

And finally

$$c = 1.593a = (1.593)(0.323 \text{ nm}) = 0.515 \text{ nm}$$

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3.12 *Using atomic weight, crystal structure, and atomic radius data tabulated inside the front cover, compute the theoretical densities of lead, chromium, copper, and cobalt, and then compare these values with the measured densities listed in this same table. The c/a ratio for cobalt is 1.623.*

Solution

Since Pb has an FCC crystal structure, $n = 4$, and $V_C = 16R^3\sqrt{2}$ (Equation 3.4). Also, $R = 0.175$ nm (1.75×10^{-8} cm) and $A_{Pb} = 207.2$ g/mol. Employment of Equation 3.5 yields

$$\rho = \frac{nA_{Pb}}{V_C N_A}$$

$$= \frac{(4 \text{ atoms/unit cell})(207.2 \text{ g/mol})}{\left\{\left[(16)\left(1.75 \times 10^{-8} \text{ cm}\right)^3\left(\sqrt{2}\right)\right]/(\text{unit cell})\right\}\left(6.022 \times 10^{23} \text{ atoms/mol}\right)}$$

$$= 11.35 \text{ g/cm}^3$$

The value given in the table inside the front cover is 11.35 g/cm^3.

Chromium has a BCC crystal structure for which $n = 2$ and $V_C = a^3 = \left(\frac{4R}{\sqrt{3}}\right)^3$ (Equation 3.3); also $A_{Cr} = 52.00$g/mol and $R = 0.125$ nm. Therefore, employment of Equation 3.5 leads to

$$\rho = \frac{(2 \text{ atoms/unit cell})(52.00 \text{ g/mol})}{\left\{\left[\frac{(4)\left(1.25 \times 10^{-8} \text{ cm}\right)}{\sqrt{3}}\right]^3/(\text{unit cell})\right\}\left(6.022 \times 10^{23} \text{ atoms/mol}\right)}$$

$$= 7.18 \text{ g/cm}^3$$

The value given in the table is 7.19 g/cm^3.

Copper also has an FCC crystal structure and therefore

$$\rho = \frac{(4 \text{ atoms/unit cell})(63.55 \text{ g/mol})}{\left\{\left[(2)\left(1.28 \times 10^{-8} \text{ cm}\right)\left(\sqrt{2}\right)\right]^3/(\text{unit cell})\right\}\left(6.022 \times 10^{23} \text{ atoms/mol}\right)}$$

$$= 8.90 \text{ g/cm}^3$$

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The value given in the table is 8.90 g/cm^3.

Cobalt has an HCP crystal structure, and from the solution to Problem 3.6 (Equation 3.S1),

$$V_C = 6R^2c\sqrt{3}$$

and, since $c = 1.623a$ and $a = 2R$, $c = (1.623)(2R)$; hence

$$V_C = 6R^2(1.623)(2R)\sqrt{3} = (19.48)(\sqrt{3})R^3$$

$$= (19.48)(\sqrt{3})(1.25 \times 10^{-8}\ \text{cm})^3$$

$$= 6.59 \times 10^{-23}\ \text{cm}^3/\text{unit cell}$$

Also, there are 6 atoms/unit cell for HCP. Therefore the theoretical density is

$$\rho = \frac{nA_{\text{Co}}}{V_C N_{\text{A}}}$$

$$= \frac{(6\ \text{atoms/unit cell})(58.93\ \text{g/mol})}{\left(6.59 \times 10^{-23}\ \text{cm}^3/\text{unit cell}\right)\left(6.022 \times 10^{23}\ \text{atoms/mol}\right)}$$

$$= 8.91\ \text{g/cm}^3$$

The value given in the table is 8.9 g/cm^3.

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3.13 *Rhodium has an atomic radius of 0.1345 nm and a density of 12.41 g/cm^3. Determine whether it has an FCC or BCC crystal structure.*

Solution

In order to determine whether Rh has an FCC or a BCC crystal structure, we need to compute its density for each of the crystal structures. For FCC, $n = 4$, and $a = 2R\sqrt{2}$ (Equation 3.1). Also, from Figure 2.6, its atomic weight is 102.91 g/mol. Thus, for FCC (employing Equation 3.5)

$$\rho = \frac{nA_{Rh}}{a^3 N_A} = \frac{nA_{Rh}}{(2R\sqrt{2})^3 N_A}$$

$$= \frac{(4 \text{ atoms/unit cell})(102.91 \text{ g/mol})}{\left\{\left[(2)(1.345 \times 10^{-8} \text{ cm})(\sqrt{2})\right]^3 /(\text{unit cell})\right\}(6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 12.41 \text{ g/cm}^3$$

which is the value provided in the problem statement. Therefore, Rh has the FCC crystal structure.

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3.14 *Below are listed the atomic weight, density, and atomic radius for three hypothetical alloys. For each determine whether its crystal structure is FCC, BCC, or simple cubic and then justify your determination. A simple cubic unit cell is shown in Figure 3.24.*

Alloy	***Atomic Weight* (*g/mol*)**	***Density* (*g/cm*^{3})**	***Atomic Radius* (*nm*)**
A	*77.4*	*8.22*	*0.125*
B	*107.6*	*13.42*	*0.133*
C	*127.3*	*9.23*	*0.142*

Solution

For each of these three alloys we need, by trial and error, to calculate the density using Equation 3.5, and compare it to the value cited in the problem. For SC, BCC, and FCC crystal structures, the respective values of n are 1, 2, and 4, whereas the expressions for a (since $V_C = a^3$) are $2R$, $2R\sqrt{2}$, and $\frac{4R}{\sqrt{3}}$.

For alloy A, let us calculate ρ assuming a simple cubic crystal structure.

$$\rho = \frac{nA_A}{V_C N_A}$$

$$= \frac{nA_A}{(2R)^3 N_A}$$

$$= \frac{(1 \text{ atom/unit cell})(77.4 \text{ g/mol})}{\left\{\left[(2)(1.25 \times 10^{-8})\right]^3 \text{/(unit cell)}\right\}(6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 8.22 \text{ g/cm}^3$$

Therefore, its crystal structure is simple cubic.

For alloy B, let us calculate ρ assuming an FCC crystal structure.

$$\rho = \frac{nA_B}{(2R\sqrt{2})^3 N_A}$$

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$$= \frac{(4 \text{ atoms/unit cell})(107.6 \text{ g/mol})}{\left\{\left[\left(2\sqrt{2}\right)\left(1.33 \times 10^{-8} \text{ cm}\right)\right]^3/(\text{unit cell})\right\}\left(6.022 \times 10^{23} \text{ atoms/mol}\right)}$$

$$= 13.42 \text{ g/cm}^3$$

Therefore, its crystal structure is FCC.

For alloy C, let us calculate ρ assuming a simple cubic crystal structure.

$$= \frac{nA_C}{(2R)^3 N_A}$$

$$= \frac{(1 \text{ atom/unit cell})(127.3 \text{ g/mol})}{\left\{\left[(2)\left(1.42 \times 10^{-8} \text{ cm}\right)\right]^3/(\text{unit cell})\right\}\left(6.022 \times 10^{23} \text{ atoms/mol}\right)}$$

$$= 9.23 \text{ g/cm}^3$$

Therefore, its crystal structure is simple cubic.

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3.15 *The unit cell for tin has tetragonal symmetry, with a and b lattice parameters of 0.583 and 0.318 nm, respectively. If its density, atomic weight, and atomic radius are 7.30 g/cm^3, 118.69 g/mol, and 0.151 nm, respectively, compute the atomic packing factor.*

Solution

In order to determine the APF for Sn, we need to compute both the unit cell volume (V_C) which is just the a^2c product, as well as the total sphere volume (V_S) which is just the product of the volume of a single sphere and the number of spheres in the unit cell (n). The value of n may be calculated from Equation 3.5 as

$$n = \frac{\rho V_C N_A}{A_{Sn}}$$

$$= \frac{(7.30 \text{ g/cm}^3)(5.83)^2(3.18)(\times 10^{-24} \text{ cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})}{118.69 \text{ g/mol}}$$

$$= 4.00 \text{ atoms/unit cell}$$

Therefore

$$\text{APF} = \frac{V_S}{V_C} = \frac{(4)\left(\frac{4}{3}\pi R^3\right)}{(a)^2(c)}$$

$$= \frac{(4)\left[\frac{4}{3}(\pi)(1.51 \times 10^{-8} \text{ cm})^3\right]}{(5.83 \times 10^{-8} \text{ cm})^2(3.18 \times 10^{-8} \text{ cm})}$$

$$= 0.534$$

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3.16 *Iodine has an orthorhombic unit cell for which the a, b, and c lattice parameters are 0.479, 0.725, and 0.978 nm, respectively.*

(a) If the atomic packing factor and atomic radius are 0.547 and 0.177 nm, respectively, determine the number of atoms in each unit cell.

(b) The atomic weight of iodine is 126.91 g/mol; compute its theoretical density.

Solution

(a) For indium, and from the definition of the APF

$$\text{APF} = \frac{V_S}{V_C} = \frac{n\left(\frac{4}{3}\pi R^3\right)}{abc}$$

we may solve for the number of atoms per unit cell, n, as

$$n = \frac{(\text{APF})\,abc}{\frac{4}{3}\pi R^3}$$

Incorporating values of the above parameters provided in the problem state leads to

$$= \frac{(0.547)(4.79 \times 10^{-8}\ \text{cm})(7.25 \times 10^{-8}\ \text{cm})\left(9.78 \times 10^{-8}\ \text{cm}\right)}{\frac{4}{3}\pi\left(1.77 \times 10^{-8}\ \text{cm}\right)^3}$$

$$= 8.0 \text{ atoms/unit cell}$$

(b) In order to compute the density, we just employ Equation 3.5 as

$$\rho = \frac{nA_{\text{I}}}{abc\,N_{\text{A}}}$$

$$= \frac{(8 \text{ atoms/unit cell})(126.91 \text{ g/mol})}{\left\{\left[(4.79 \times 10^{-8}\ \text{cm})(7.25 \times 10^{-8}\ \text{cm})\left(9.78 \times 10^{-8}\ \text{cm}\right)\right]/\text{unit cell}\right\}\left(6.022 \times 10^{23}\ \text{atoms/mol}\right)}$$

$$= 4.96\ \text{g/cm}^3$$

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3. 17 *Titanium has an HCP unit cell for which the ratio of the lattice parameters c/a is 1.58. If the radius of the Ti atom is 0.1445 nm, (a) determine the unit cell volume, and (b) calculate the density of Ti and compare it with the literature value.*

Solution

(a) We are asked to calculate the unit cell volume for Ti. For HCP, from Equation 3.S1 (found in the solution to Problem 3.6)

$$V_C = 6R^2c\sqrt{3}$$

But for Ti, $c = 1.58a$, and $a = 2R$, or $c = 3.16R$, and

$$V_C = (6)(3.16)\, R^3\sqrt{3}$$

$$= (6)(3.16)\left(\sqrt{3}\right)\left[1.445 \times 10^{-8}\ \text{cm}\right]^3 = 9.91 \times 10^{-23}\ \text{cm}^3/\text{unit cell}$$

(b) The theoretical density of Ti is determined, using Equation 3.5, as follows:

$$\rho = \frac{nA_{\text{Ti}}}{V_C N_{\text{A}}}$$

For HCP, $n = 6$ atoms/unit cell, and for Ti, $A_{\text{Ti}} = 47.87$ g/mol (as noted inside the front cover). Thus,

$$\rho = \frac{(6\ \text{atoms/unit cell})(47.87\ \text{g/mol})}{\left(9.91 \times 10^{-23}\ \text{cm}^3/\text{unit cell}\right)\left(6.022 \times 10^{23}\ \text{atoms/mol}\right)}$$

$$= 4.81\ \text{g/cm}^3$$

The value given in the literature is 4.51 g/cm^3.

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3.18 *Zinc has an HCP crystal structure, a c/a ratio of 1.856, and a density of 7.13 g/cm^3. Compute the atomic radius for Zn.*

Solution

In order to calculate the atomic radius for Zn, we must use Equation 3.5, as well as the expression which relates the atomic radius to the unit cell volume for HCP; Equation 3.S1 (from Problem 3.6) is as follows:

$$V_C = 6R^2c\sqrt{3}$$

In this case $c = 1.856a$, but, for HCP, $a = 2R$, which means that

$$V_C = 6R^2(1.856)(2R)\sqrt{3} = (1.856)(12\sqrt{3})R^3$$

And from Equation 3.5, the density is equal to

$$\rho = \frac{nA_{Zn}}{V_C N_A} = \frac{nA_{Zn}}{(1.856)(12\sqrt{3})R^3 N_A}$$

And, solving for R from the above equation leads to the following:

$$R = \left[\frac{nA_{Zn}}{(1.856)(12\sqrt{3})\,\rho\, N_A}\right]^{1/3}$$

And incorporating appropriate values for the parameters in this equation leads to

$$R = \left[\frac{(6 \text{ atoms/unit cell})\,(65.41 \text{ g/mol})}{(1.856)(12\sqrt{3})(7.13 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})}\right]^{1/3}$$

$$= 1.33 \times 10^{-8} \text{ cm} = 0.133 \text{ nm}$$

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3.19 *Rhenium has an HCP crystal structure, an atomic radius of 0.137 nm, and a c/a ratio of 1.615. Compute the volume of the unit cell for Re.*

Solution

In order to compute the volume of the unit cell for Re, it is necessary to use Equation 3.S1 (found in Problem 3.6), that is

$$V_C = 6R^2c\sqrt{3}$$

The problem states that $c = 1.615a$, and $a = 2R$. Therefore

$$V_C = (1.615)\left(12\sqrt{3}\right) R^3$$

$$= (1.615)\left(12\sqrt{3}\right)(1.37 \times 10^{-8}\ \text{cm})^3 = 8.63 \times 10^{-23}\ \text{cm}^3 = 8.63 \times 10^{-2}\ \text{nm}^3$$

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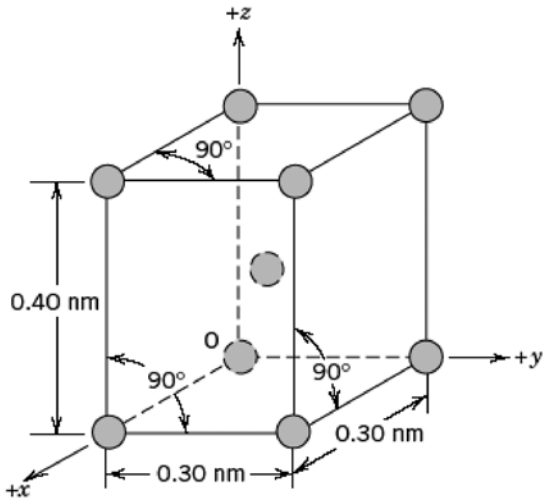
Crystal Systems

3.20 *Below is a unit cell for a hypothetical metal.*

(a) To which crystal system does this unit cell belong?

(b) What would this crystal structure be called?

(c) Calculate the density of the material, given that its atomic weight is 141 g/mol.



Solution

(a) The unit cell shown in the problem statement belongs to the tetragonal crystal system since $a = b =$ 0.30 nm, $c = 0.40$ nm, and $\alpha = \beta = \gamma = 90°$.

(b) The crystal structure would be called *body-centered tetragonal*.

(c) As with BCC, $n = 2$ atoms/unit cell. Also, for this unit cell

$$V_C = (3.0 \times 10^{-8}\ \text{cm})^2(4.0 \times 10^{-8}\ \text{cm})$$

$$= 3.60 \times 10^{-23}\ \text{cm}^3/\text{unit cell}$$

Thus, using Equation 3.5, the density is equal to

$$\rho = \frac{nA}{V_C N_A}$$

$$= \frac{(2\ \text{atoms/unit cell})\,(141\ \text{g/mol})}{(3.60 \times 10^{-23}\ \text{cm}^3/\text{unit cell})(6.022 \times 10^{23}\ \text{atoms/mol})}$$

$$= 13.0\ \text{g/cm}^3$$

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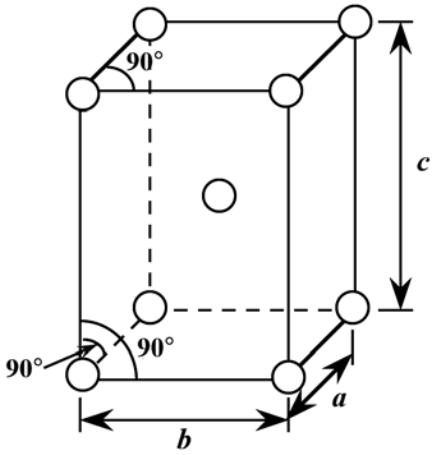
3.21 *Sketch a unit cell for the body-centered orthorhombic crystal structure.*

Solution

A unit cell for the body-centered orthorhombic crystal structure is presented below.



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Point Coordinates

3.22 *List the point coordinates for all atoms that are associated with the FCC unit cell (Figure 3.1).*

Solution

From Figure 3.1b, the atom located of the origin of the unit cell has the coordinates 000. Coordinates for other atoms in the bottom face are 100, 110, 010, and $\frac{1}{2}\frac{1}{2}0$. (The *z* coordinate for all these points is zero.)

For the top unit cell face, the coordinates are 001, 101, 111, 011, and $\frac{1}{2}\frac{1}{2}1$.

Coordinates for those atoms that are positioned at the centers of both side faces, and centers of both front and back faces need to be specified. For the front and back-center face atoms, the coordinates are $1\frac{1}{2}\frac{1}{2}$ and $0\frac{1}{2}\frac{1}{2}$, respectively. While for the left and right side center-face atoms, the respective coordinates are $\frac{1}{2}0\frac{1}{2}$ and $\frac{1}{2}1\frac{1}{2}$.

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3.23 *List the point coordinates of the titanium, barium, and oxygen ions for a unit cell of the perovskite crystal structure (Figure 12.6).*

Solution

In Figure 12.6, the barium ions are situated at all corner positions. The point coordinates for these ions are as follows: 000, 100, 110, 010, 001, 101, 111, and 011.

The oxygen ions are located at all face-centered positions; therefore, their coordinates are $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}1$, $1\frac{1}{2}\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, and $\frac{1}{2}1\frac{1}{2}$.

And, finally, the titanium ion resides at the center of the cubic unit cell, with coordinates $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

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3.24 *List the point coordinates of all atoms that are associated with the diamond cubic unit cell (Figure 12.15).*

Solution

First of all, one set of carbon atoms occupy all corner positions of the cubic unit cell; the coordinates of these atoms are as follows: 000, 100, 110, 010, 001, 101, 111, and 011.

Another set of atoms reside on all of the face-centered positions, with the following coordinates: $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}1$, $1\frac{1}{2}\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, and $\frac{1}{2}1\frac{1}{2}$.

The third set of carbon atoms are positioned within the interior of the unit cell. Using an *x*-*y*-*z* coordinate system oriented as in Figure 3.4, the coordinates of the atom that lies toward the lower-left-front of the unit cell has the coordinates $\frac{3}{4}\frac{1}{4}\frac{1}{4}$, whereas the atom situated toward the lower-right-back of the unit cell has coordinates of $\frac{1}{4}\frac{3}{4}\frac{1}{4}$. Also, the carbon atom that resides toward the upper-left-back of the unit cell has the $\frac{1}{4}\frac{1}{4}\frac{3}{4}$ coordinates. And, the coordinates of the final atom, located toward the upper-right-front of the unit cell, are $\frac{3}{4}\frac{3}{4}\frac{3}{4}$.

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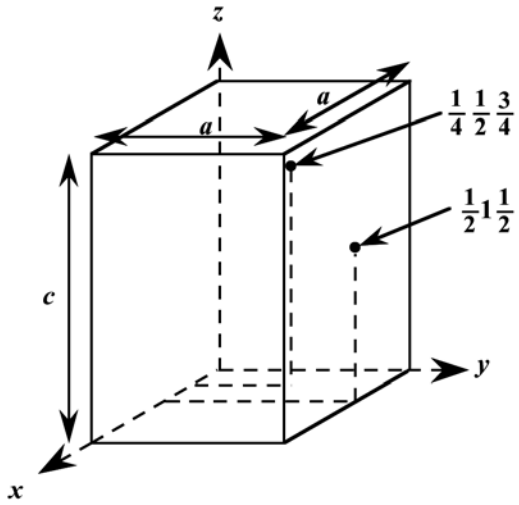
3.25 *Sketch a tetragonal unit cell , and within that cell indicate locations of the* $\frac{1}{2}$ 1 $\frac{1}{2}$ *and* $\frac{1}{4}$ $\frac{1}{2}$ $\frac{3}{4}$ *point coordinates.*

Solution

A tetragonal unit in which are shown the $\frac{1}{2}$ 1 $\frac{1}{2}$ and $\frac{1}{4}\frac{1}{2}\frac{3}{4}$ point coordinates is presented below.



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3.26 *Using the Molecule Definition Utility found in both "Metallic Crystal Structures and Crystallography" and "Ceramic Crystal Structures" modules of VMSE, located on the book's web site [www.wiley.com/college/Callister (Student Companion Site)], generate a three-dimensional unit cell for the intermetallic compound $AuCu_3$ given the following: (1) the unit cell is cubic with an edge length of 0.374 nm, (2) gold atoms are situated at all cube corners, and (3) copper atoms are positioned at the centers of all unit cell faces.*

Solution

First of all, open the "Molecular Definition Utility"; it may be found in either of "Metallic Crystal Structures and Crystallography" or "Ceramic Crystal Structures" modules.

In the "Step 1" window, it is necessary to define the atom types, colors for the spheres (atoms), and specify atom sizes. Let us enter "Au" as the name for the gold atoms (since "Au" the symbol for gold), and "Cu" as the name for the copper atoms. Next it is necessary to choose a color for each atom type from the selections that appear in the pull-down menu—for example, "Yellow" for Au and "Red" for Cu. In the "Atom Size" window, it is necessary to enter an atom/ion size. In the instructions for this step, it is suggested that the atom/ion diameter in nanometers be used. From the table found inside the front cover of the textbook, the atomic radii for gold and copper are 0.144 nm and 0.128 nm, respectively, and, therefore, their ionic diameters are twice these values (i.e., 0.288 nm and 0.256 nm); therefore, we enter the values "0.288" and "0.256" for the two atom types. Now click on the "Register" button, followed by clicking on the "Go to Step 2" button.

In the "Step 2" window we specify positions for all of the atoms within the unit cell; their point coordinates are specified in the problem statement. Let's begin with gold. Click on the yellow sphere that is located to the right of the "Molecule Definition Utility" box. Again, Au atoms are situated at all eight corners of the cubic unit cell. One Au will be positioned at the origin of the coordinate system—i.e., its point coordinates are 000, and, therefore, we enter a "0" (zero) in each of the "x", "y", and "z" atom position boxes. Next we click on the "Register Atom Position" button. Now we enter the coordinates of another gold atom; let us arbitrarily select the one that resides at the corner of the unit cell that is one unit-cell length along the *x*-axis (i.e., at the 100 point coordinate). Inasmuch as it is located a distance of *a* units along the *x*-axis the value of "0.374" is entered in the "x" atom position box (since this is the value of *a* given in the problem statement); zeros are entered in each of the "y" and "z" position boxes. We repeat this procedure for the remaining six Au atoms.

After this step has been completed, it is necessary to specify positions for the copper atoms, which are located at all six face-centered sites. To begin, we click on the red sphere that is located next to the "Molecule Definition Utility" box. The point coordinates for some of the Cu atoms are fractional ones; in these instances, the *a* unit cell length (i.e., 0.374) is multiplied by the fraction. For example, one Cu atom is located $1\frac{1}{2}\frac{1}{2}$ coordinate. Therefore, the x, y, and z atoms positions are (1)(0.374) = 0.374, $\frac{1}{2}$(0.374) = 0.187, and $\frac{1}{2}$(0.374) = 0.187, respectively.

For the gold atoms, the x, y, and z atom position entries for all 8 sets of point coordinates are as follows:

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0, 0, and 0

0.374, 0, and 0

0, 0.374, and 0

0, 0, and 0.374

0, 0.374, 0.374

0.374, 0, 0.374

0.374, 0.374, 0

0.374, 0.374, 0.374

Now, for the copper atoms, the x, y, and z atom position entries for all 6 sets of point coordinates are as follows:

0.187, 0.187, 0

0.187, 0, 0.187

0, 0.187, 0.187

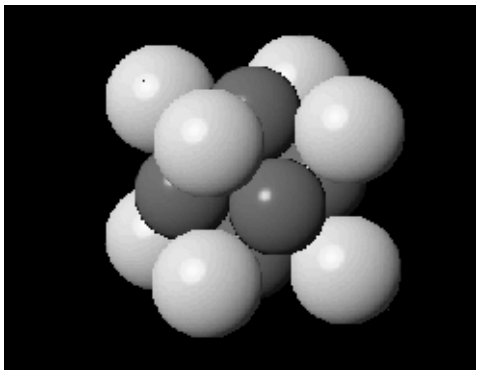
0.374, 0.187, 0.187

0.187, 0.374, 0.187

0.187, 0.187, 0.374

In Step 3, we may specify which atoms are to be represented as being bonded to one another, and which type of bond(s) to use (single solid, single dashed, double, and triple are possibilities), or we may elect to not represent any bonds at all (in which case we are finished). If it is decided to show bonds, probably the best thing to do is to represent unit cell edges as bonds. This image may be rotated by using mouse click-and-drag

Your image should appear as the following screen shot. Here the gold atoms appear lighter than the copper atoms.



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[Note: Unfortunately, with this version of the Molecular Definition Utility, it is not possible to save either the data or the image that you have generated. You may use screen capture (or screen shot) software to record and store your image.]

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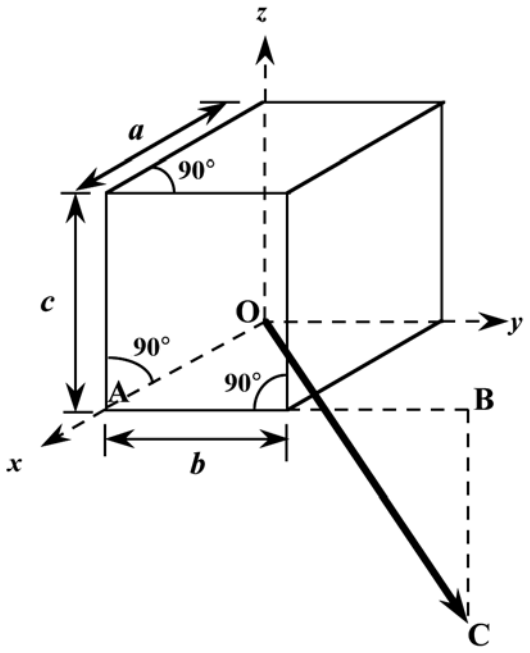
Crystallographic Directions

3.27 *Draw an orthorhombic unit cell, and within that cell a* $[12\bar{1}]$ *direction.*

Solution

This problem calls for us to draw a $[12\bar{1}]$ direction within an orthorhombic unit cell ($a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$). Such a unit cell with its origin positioned at point O is shown below. We first move along the +*x*-axis *a* units (from point O to point A), then parallel to the +*y*-axis 2*b* units (from point A to point B). Finally, we proceed parallel to the *z*-axis -*c* units (from point B to point C). The $[12\bar{1}]$ direction is the vector from the origin (point O) to point C as shown.



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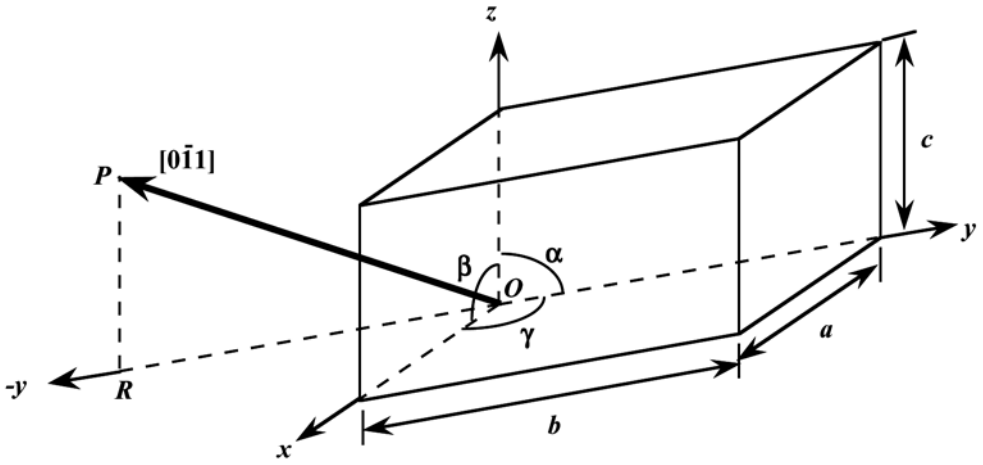
3.28 *Sketch a monoclinic unit cell, and within that cell a* $[0\bar{1}1]$ *direction.*

Solution

This problem asks that a $[0\bar{1}1]$ direction be drawn within a monoclinic unit cell ($a \neq b \neq c$, and $\alpha = \beta = 90^\circ \neq \gamma$). One such unit cell with its origin at point *O* is sketched below. For this direction, there is no projection along the *x*-axis since the first index is zero; thus, the direction lies in the *y*-*z* plane. We next move from the origin along the minus *y*-axis *b* units (from point *O* to point *R*). Since the final index is a one, move from point *R* parallel to the *z*-axis, *c* units (to point *P*). Thus, the $[0\bar{1}1]$ direction corresponds to the vector passing from the origin (point *O*) to point *P*, as indicated in the figure.



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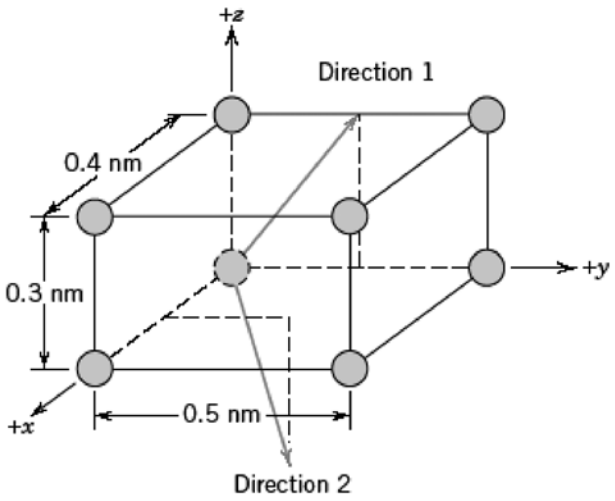
3.29 *What are the indices for the directions indicated by the two vectors in the sketch below?*



Solution

For direction 1, the projection on the *x*-axis is zero (since it lies in the *y*-*z* plane), while projections on the *y*- and *z*-axes, *b*/2 and *c*, respectively. This is a [012] direction as indicated in the summary below.

	x	*y*	*z*
Projections	0*a*	*b*/2	*c*
Projections in terms of *a*, *b*, and *c*	0	1/2	1
Reduction to integers	0	1	2
Enclosure		[012]	

Direction 2 is $[11\bar{2}]$ as summarized below.

	x	*y*	*z*
Projections	*a*/2	*b*/2	-*c*
Projections in terms of *a*, *b*, and *c*	1/2	1/2	-1
Reduction to integers	1	1	-2
Enclosure		$[11\bar{2}]$	

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3.30 *Within a cubic unit cell, sketch the following directions:*

(a) $[\bar{1}10]$, *(e)* $[\bar{1}\bar{1}1]$,

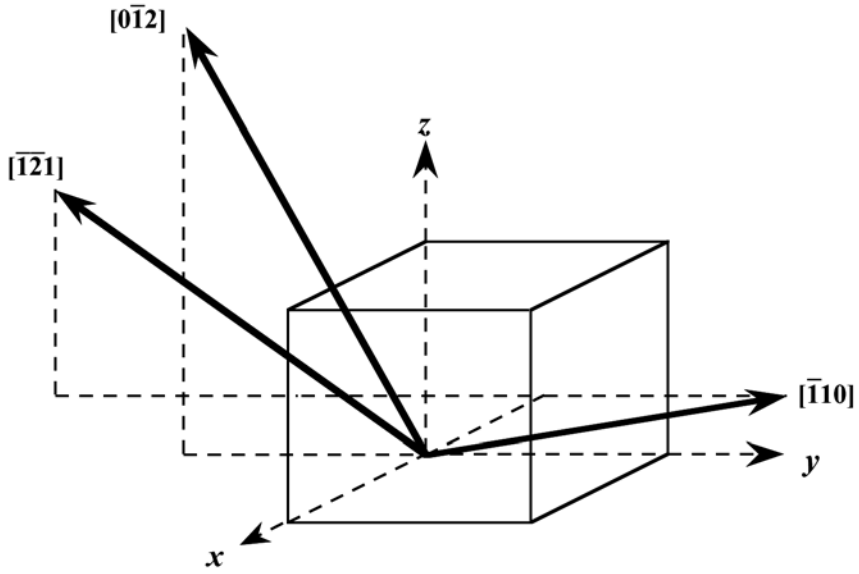
(b) $[\bar{1}\bar{2}1]$, *(f)* $[\bar{1}22]$,

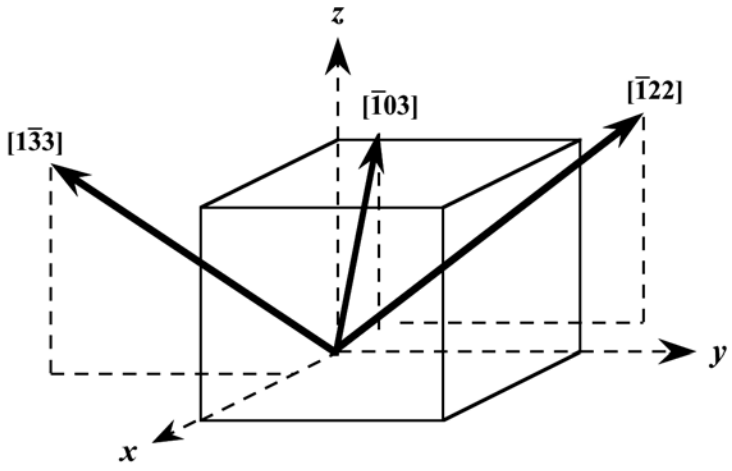
(c) $[0\bar{1}2]$, *(g)* $[12\bar{3}]$,

(d) $[1\bar{3}3]$, *(h)* $[\bar{1}03]$.

Solution

The directions asked for are indicated in the cubic unit cells shown below.





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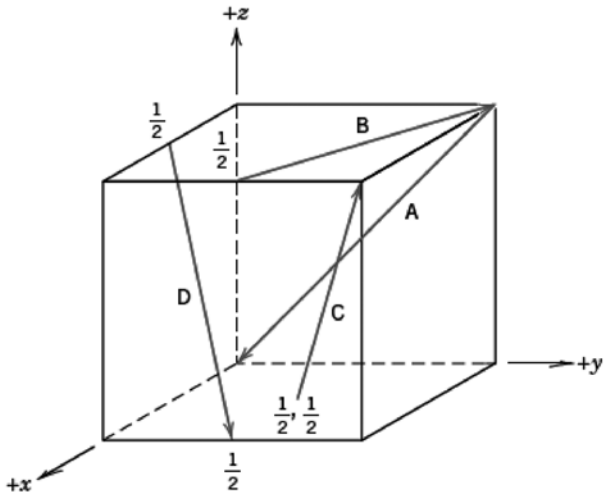
3.31 *Determine the indices for the directions shown in the following cubic unit cell:*



Solution

Direction A is a $[0\bar{1}\bar{1}]$direction, which determination is summarized as follows. We first of all position the origin of the coordinate system at the tail of the direction vector; then in terms of this new coordinate system

	x	*y*	*z*
Projections	0*a*	–*b*	–*c*
Projections in terms of *a*, *b*, and *c*	0	–1	–1
Reduction to integers		not necessary	
Enclosure		$[0\bar{1}\bar{1}]$	

Direction B is a $[\bar{2}10]$ direction, which determination is summarized as follows. We first of all position the origin of the coordinate system at the tail of the direction vector; then in terms of this new coordinate system

	x	*y*	*z*
Projections	–*a*	$\frac{b}{2}$	0*c*
Projections in terms of *a*, *b*, and *c*	–1	$\frac{1}{2}$	0
Reduction to integers	–2	1	0
Enclosure		$[\bar{2}10]$	

Direction C is a [112] direction, which determination is summarized as follows. We first of all position the origin of the coordinate system at the tail of the direction vector; then in terms of this new coordinate system

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	x	y	z
Projections	$\frac{a}{2}$	$\frac{b}{2}$	c
Projections in terms of a, b, and c	$\frac{1}{2}$	$\frac{1}{2}$	1
Reduction to integers	1	1	2
Enclosure		[112]	

Direction D is a $[11\bar{2}]$ direction, which determination is summarized as follows. We first of all position the origin of the coordinate system at the tail of the direction vector; then in terms of this new coordinate system

	x	y	z
Projections	$\frac{a}{2}$	$\frac{b}{2}$	$-c$
Projections in terms of a, b, and c	$\frac{1}{2}$	$\frac{1}{2}$	-1
Reduction to integers	1	1	-2
Enclosure		$[11\bar{2}]$	

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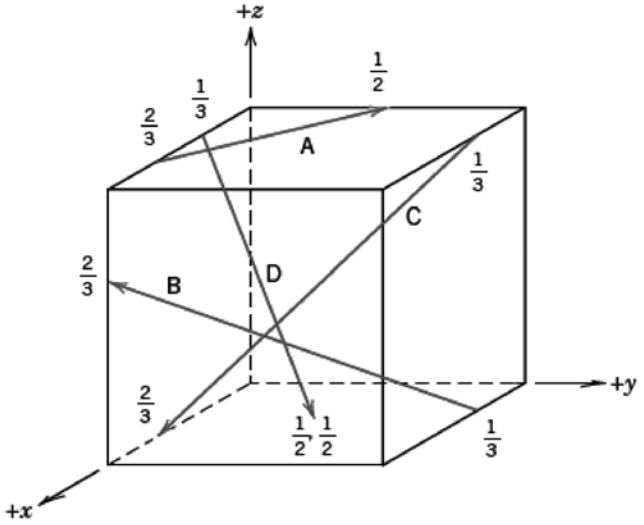
3.32 *Determine the indices for the directions shown in the following cubic unit cell:*



Solution

Direction A is a $[\bar{4}30]$ direction, which determination is summarized as follows. We first of all position the origin of the coordinate system at the tail of the direction vector; then in terms of this new coordinate system

	x	y	z
Projections	$-\frac{2a}{3}$	$\frac{b}{2}$	$0c$
Projections in terms of a, b, and c	$-\frac{2}{3}$	$\frac{1}{2}$	0
Reduction to integers	–4	3	0
Enclosure		$[\bar{4}30]$	

Direction B is a $[2\bar{3}2]$ direction, which determination is summarized as follows. We first of all position the origin of the coordinate system at the tail of the direction vector; then in terms of this new coordinate system

	x	y	z
Projections	$\frac{2a}{3}$	$-b$	$\frac{2c}{3}$
Projections in terms of a, b, and c	$\frac{2}{3}$	–1	$\frac{2}{3}$
Reduction to integers	2	–3	2
Enclosure		$[2\bar{3}2]$	

Direction C is a $[1\bar{3}\bar{3}]$ direction, which determination is summarized as follows. We first of all position the origin of the coordinate system at the tail of the direction vector; then in terms of this new coordinate system

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	x	y	z
Projections	$\frac{a}{3}$	$-b$	$-c$
Projections in terms of a, b, and c	$\frac{1}{3}$	-1	-1
Reduction to integers	1	-3	-3
Enclosure		$[1\bar{3}\bar{3}]$	

Direction D is a $[13\bar{6}]$ direction, which determination is summarized as follows. We first of all position the origin of the coordinate system at the tail of the direction vector; then in terms of this new coordinate system

	x	y	z
Projections	$\frac{a}{6}$	$\frac{b}{2}$	$-c$
Projections in terms of a, b, and c	$\frac{1}{6}$	$\frac{1}{2}$	-1
Reduction to integers	1	3	-6
Enclosure		$[13\bar{6}]$	

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3.33 *For tetragonal crystals, cite the indices of directions that are equivalent to each of the following directions:*

(a) [*001*]

(b) [*110*]

(c) [*010*]

Solution

For tetragonal crystals $a = b \neq c$ and $\alpha = \beta = \gamma = 90°$; therefore, projections along the *x* and *y* axes are equivalent, which are not equivalent to projections along the *z* axis.

(a) Therefore, for the [001] direction, there is only one equivalent direction: $[00\bar{1}]$.

(b) For the [110] direction, equivalent directions are as follows: $[\bar{1}\,\bar{1}0]$, $[\bar{1}10]$, and $[1\bar{1}0]$

(b) Also, for the [010] direction, equivalent directions are the following: $[0\bar{1}0]$, $[100]$, and $[\bar{1}00]$.

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3.34 *Convert the* [*100*] and [*111*] *directions into the four-index Miller–Bravais scheme for hexagonal unit cells.*

Solution

For [100]

$u' = 1,$

$v' = 0,$

$w' = 0$

From Equations 3.6

$$u = \frac{1}{3}(2u' - v') = \frac{1}{3}[(2)(1) - 0] = \frac{2}{3}$$

$$v = \frac{1}{3}(2v' - u') = \frac{1}{3}[(2)(0) - 1] = -\frac{1}{3}$$

$$t = -(u + v) = -\left(\frac{2}{3} - \frac{1}{3}\right) = -\frac{1}{3}$$

$$w = w' = 0$$

It is necessary to multiply these numbers by 3 in order to reduce them to the lowest set of integers. Thus, the direction is represented as $[uvtw] = [2\bar{1}\bar{1}0]$.

For [111], $u' = 1$, $v' = 1$, and $w' = 1$; therefore,

$$u = \frac{1}{3}[(2)(1) - 1] = \frac{1}{3}$$

$$v = \frac{1}{3}[(2)(1) - 1] = \frac{1}{3}$$

$$t = -\left(\frac{1}{3} + \frac{1}{3}\right) = -\frac{2}{3}$$

$$w = 1$$

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If we again multiply these numbers by 3, then $u = 1$, $v = 1$, $t = -2$, and $w = 3$. Thus, the direction is represented as Thus, the direction is represented as $[uvtw] = [11\bar{2}3]$.

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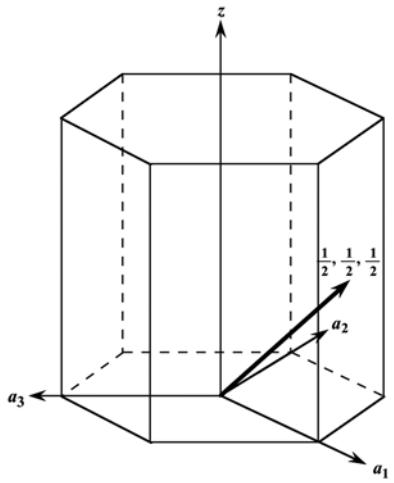
3.35 *Determine indices for the directions shown in the following hexagonal unit cells:*

Solution



(*a*)

(a) For this direction, projections on the a_1, a_2, and z axes are a, $a/2$, and $c/2$, or, in terms of a and c the projections are 1, 1/2, and 1/2, which when multiplied by the factor 2 become the smallest set of integers: 2, 1, and 1. This means that

$u' = 2$

$v' = 1$

$w' = 1$

Now, from Equations 3.6, the u, v, t, and w indices become

$$u = \frac{1}{3}(2u' - v') = \frac{1}{3}[(2)(2) - (1)] = \frac{3}{3} = 1$$

$$v = \frac{1}{3}(2v' - u') = \frac{1}{3}[(2)(1) - (2)] = 0$$

$$t = -(u + v) = -(1 + 0) = -1$$

$$w = w' = 1$$

No reduction is necessary inasmuch as all of these indices are integers; therefore, this direction in the four-index scheme is $[10\bar{1}1]$

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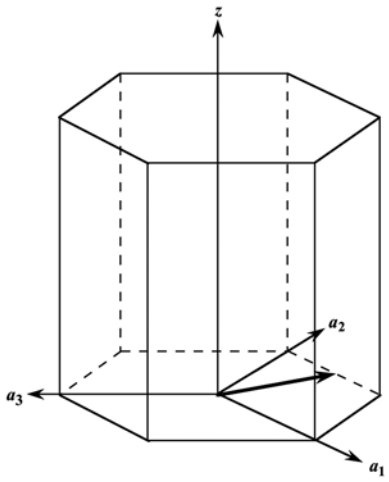

(b)

(b) For this direction, projections on the a_1, a_2, and z axes are $a/2$, a, and $0c$, or, in terms of a and c the projections are 1/2, 1, and 0, which when multiplied by the factor 2 become the smallest set of integers: 1, 2, and 0 This means that

$$u' = 1$$

$$v' = 2$$

$$w' = 0$$

Now, from Equations 3.6, the u, v, t, and w indices become

$$u = \frac{1}{3}(2u' - v) = \frac{1}{3}[(2)(1) - 2] = 0$$

$$v = \frac{1}{3}(2v' - u') = \frac{1}{3}[(2)(2) - 1] = 1$$

$$t = -(u+v) = -(0 + 1) = -1$$

$$w = w' = 0$$

No reduction is necessary inasmuch as all of these indices are integers; therefore, this direction in the four-index scheme is $[01\bar{1}0]$.

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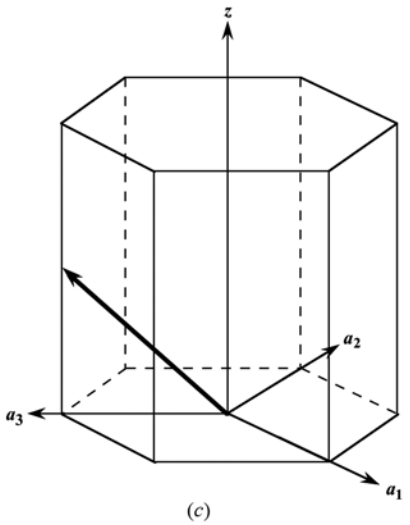

(c)

(c) For this direction projections on the a_1, a_2, and z axes are $-a$, $-a$, and $c/2$, or, in terms of a and c the projections are −1, −1, and 1/2, which when multiplied by the factor 2 become the smallest set of integers: −2, −2, and 1. This means that

$$u' = -2$$

$$v' = -2$$

$$w' = 1$$

Now, from Equations 3.6, the u, v, t, and w indices become

$$u = \frac{1}{3}(2u' - v) = \frac{1}{3}\left[(2)(-2) - (-2)\right] = -\frac{2}{3}$$

$$v = \frac{1}{3}(2v' - u') = \frac{1}{3}\left[(2)(-2) - (-2)\right] = -\frac{2}{3}$$

$$t = -(u+v) = -\left(-\frac{2}{3} - \frac{2}{3}\right) = \frac{4}{3}$$

$$w = w' = 1$$

Now, in order to get the lowest set of integers, it is necessary to multiply all indices by the factor 3, with the result that this direction is a $[\bar{2}\bar{2}43]$ direction.

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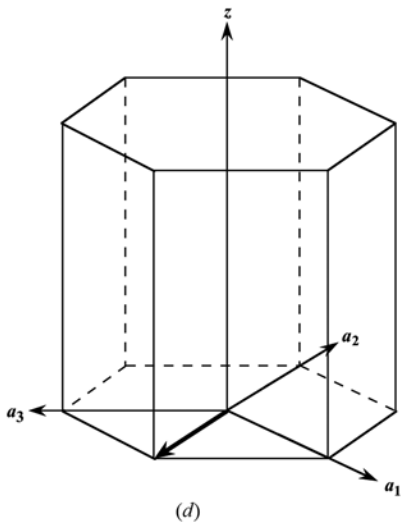

(*d*)

(d) For this direction, projections on the a_1, a_2, and z axes are $0a$, $-a$, and $0c$, or, in terms of a and c the projections are 0, -1, and 0. This means that

$$u' = 0$$

$$v' = -1$$

$$w' = 0$$

Now, from Equations 3.6, the u, v, t, and w indices become

$$u = \frac{1}{3}(2u' - v') = \frac{1}{3}[(2)(0) - (-1)] = \frac{1}{3}$$

$$v = \frac{1}{3}(2v' - u') = \frac{1}{3}[(2)(-1) - 0] = -\frac{2}{3}$$

$$t = -(u+v) = -\left(\frac{1}{3} - \frac{2}{3}\right) = \frac{1}{3}$$

$$w = w' = 0$$

Now, in order to get the lowest set of integers, it is necessary to multiply all indices by the factor 3, with the result that this is a $[1\bar{2}10]$ direction.

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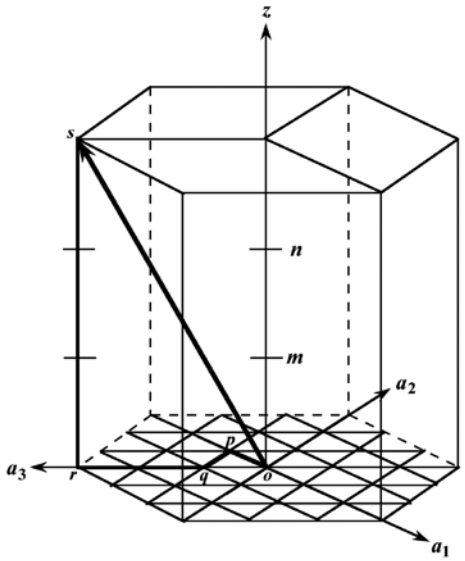
3.36 *Sketch the* $[\bar{1}\bar{1}23]$ *and* $[10\bar{1}0]$ *directions in a hexagonal unit cell.*

Solution

The first portion of this problem asks that we plot the $[\bar{1}\bar{1}23]$ within a hexagonal unit cell. Below is shown this direction plotted within a hexagonal unit cell having a reduced-scale coordinate scheme.



For this direction, projections on the a_1, a_2, a_3, and c axes are respectively, -1, -1, 2, and 3, respectively. In plotting this direction, we begin at the origin of the coordinate system, point o. From here we proceed 1 unit distance along the $-a_1$ axis (to point p), from here 1 unit distance parallel to $-a_2$ axis (to point q), then 2 unit distances parallel (or along) the a_3 axis (to point r), and finally, 3 unit distances parallel to the z axis (to point s). Thus, the $[\bar{1}\bar{1}23]$ direction is that vector that extends from point o to point s as shown.

Now we are asked to plot the $[10\bar{1}0]$ within a hexagonal unit cell. In the figure below is plotted this direction within a hexagonal unit cell having a reduced-scale coordinate scheme.

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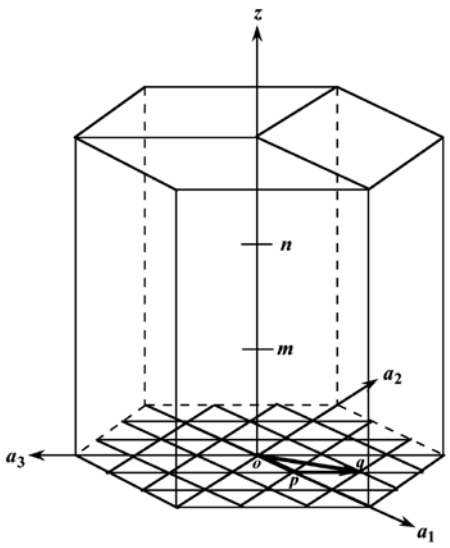

For this direction, projections on the a_1, a_2, a_3, and c axes are respectively, 1, 0, –1, and 0, respectively. In plotting this direction, we begin at the origin of the coordinate system, point o. From here we proceed 1 unit distance along the a_1 axis (to point p). Since there is no projection on the a_2 axis it is not necessary to move parallel to this axis. Therefore, from point p we proceed 1 unit distance parallel to $-a_3$ axis (to point q). And, finally, inasmuch as there is no projection along the z axis, it is not necessary to move parallel to this axis. Thus, the $[10\bar{1}0]$ direction is that vector that extends from point o to point q as shown.

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3.37 *Using Equations 3.6a, 3.6b, 3.6c, and 3.6d, derive expressions for each of the three primed indices set (u′, v′, and w′) in terms of the four unprimed indices (u, v, t, and w).*

Solution

It is first necessary to do an expansion of Equation 3.6a as

$$u = \frac{1}{3}(2u' - v) = \frac{2u'}{3} - \frac{v'}{3}$$

And solving this expression for *v'* yields

$$v' = 2u' - 3u$$

Now, substitution of this expression into Equation 3.6b gives

$$v = \frac{1}{3}(2v' - u') = \frac{1}{3}\left[(2)(2u' - 3u) - u'\right] = u' - 2u$$

Or

$$u' = v + 2u$$

And, solving for *v* from Equation 3.6c leads to

$$v = -(u + t)$$

which, when substituted into the above expression for *u'* yields

$$u' = v + 2u = -u - t + 2u = u - t$$

In solving for an expression for *v'*, we begin with the one of the above expressions for this parameter—i.e.,

$$v' = 2u' - 3u$$

Now, substitution of the above expression for *u'* into this equation leads to

$$v' = 2u' - 3u = (2)(u - t) - 3u = -u - 2t$$

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And solving for u from Equation 3.6c gives

$$u = -v - t$$

which, when substituted in the previous equation results in the following expression for v'

$$v' = -u - 2t = -(-v - t) - 2t = v - t$$

And, of course from Equation 3.6d

$$w' = w$$

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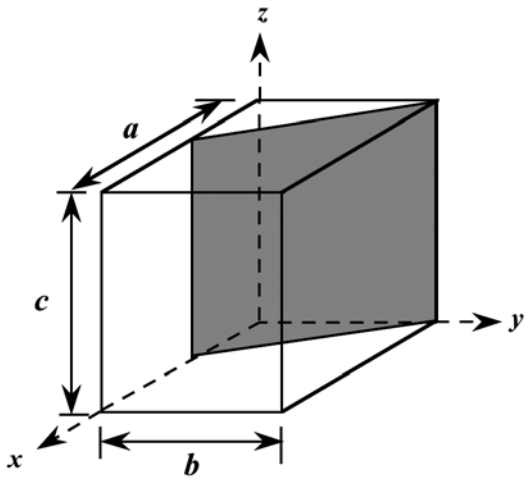
Crystallographic Planes

3.38 *(a) Draw an orthorhombic unit cell, and within that cell a (210) plane.*

(b) Draw a monoclinic unit cell, and within that cell a (002) plane.

Solution

(a) We are asked to draw a (210) plane within an orthorhombic unit cell. First remove the three indices from the parentheses, and take their reciprocals--i.e., 1/2, 1, and ∞. This means that the plane intercepts the *x*-axis at *a*/2, the *y*-axis at *b*, and parallels the *z*-axis. The plane that satisfies these requirements has been drawn within the orthorhombic unit cell below. (For orthorhombic, $a \neq b \neq c$, and $\alpha = \beta = \gamma = 90°$.)



(b) A (002) plane is drawn within the monoclinic cell shown below. We first remove the parentheses and take the reciprocals of the indices; this gives ∞, ∞, and 1/2. Thus, the (002) plane parallels both *x*- and *y*-axes, and intercepts the *z*-axis at *a*/2, as indicated in the drawing. (For monoclinic, $a \neq b \neq c$, and $\alpha = \gamma = 90° \neq \beta$.)

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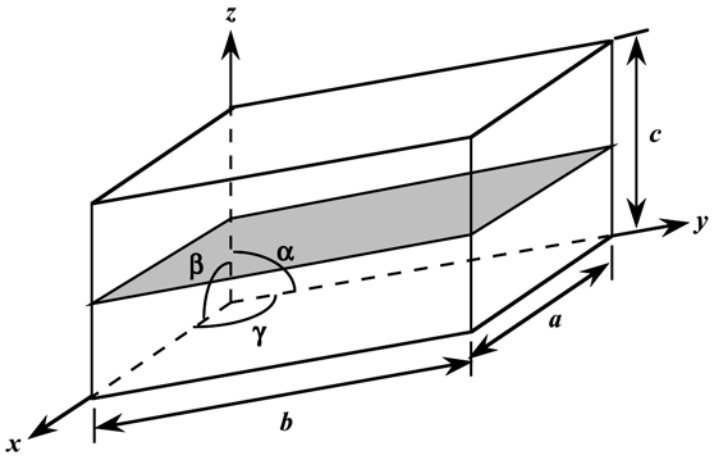

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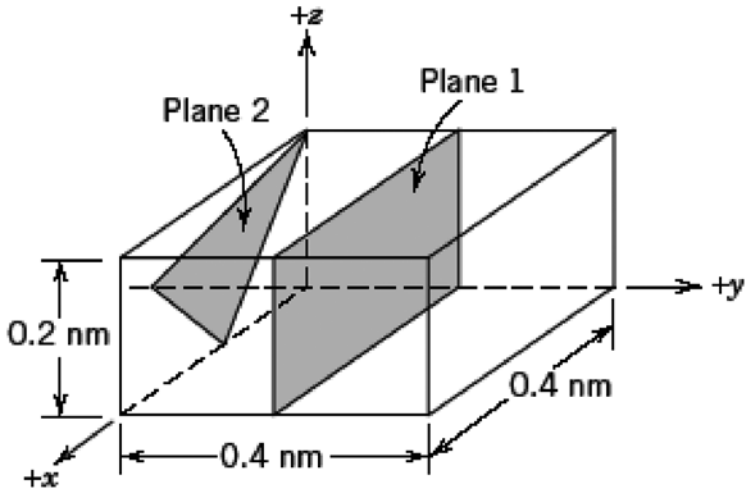
3.39 *What are the indices for the two planes drawn in the sketch below?*



Solution

Plane 1 is a (020) plane. The determination of its indices is summarized below.

	x	*y*	*z*
Intercepts	∞a	$b/2$	∞c
Intercepts in terms of *a*, *b*, and *c*	∞	1/2	∞
Reciprocals of intercepts	0	2	0
Enclosure		(020)	

Plane 2 is a $(2\bar{2}1)$ plane, as summarized below.

	x	*y*	*z*
Intercepts	$a/2$	$-b/2$	c
Intercepts in terms of *a*, *b*, and *c*	1/2	-1/2	1
Reciprocals of intercepts	2	-2	1
Enclosure		$(2\bar{2}1)$	

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3.40 *Sketch within a cubic unit cell the following planes:*

(a) $(0\bar{1}\bar{1})$, *(e)* $(\bar{1}1\bar{1})$,

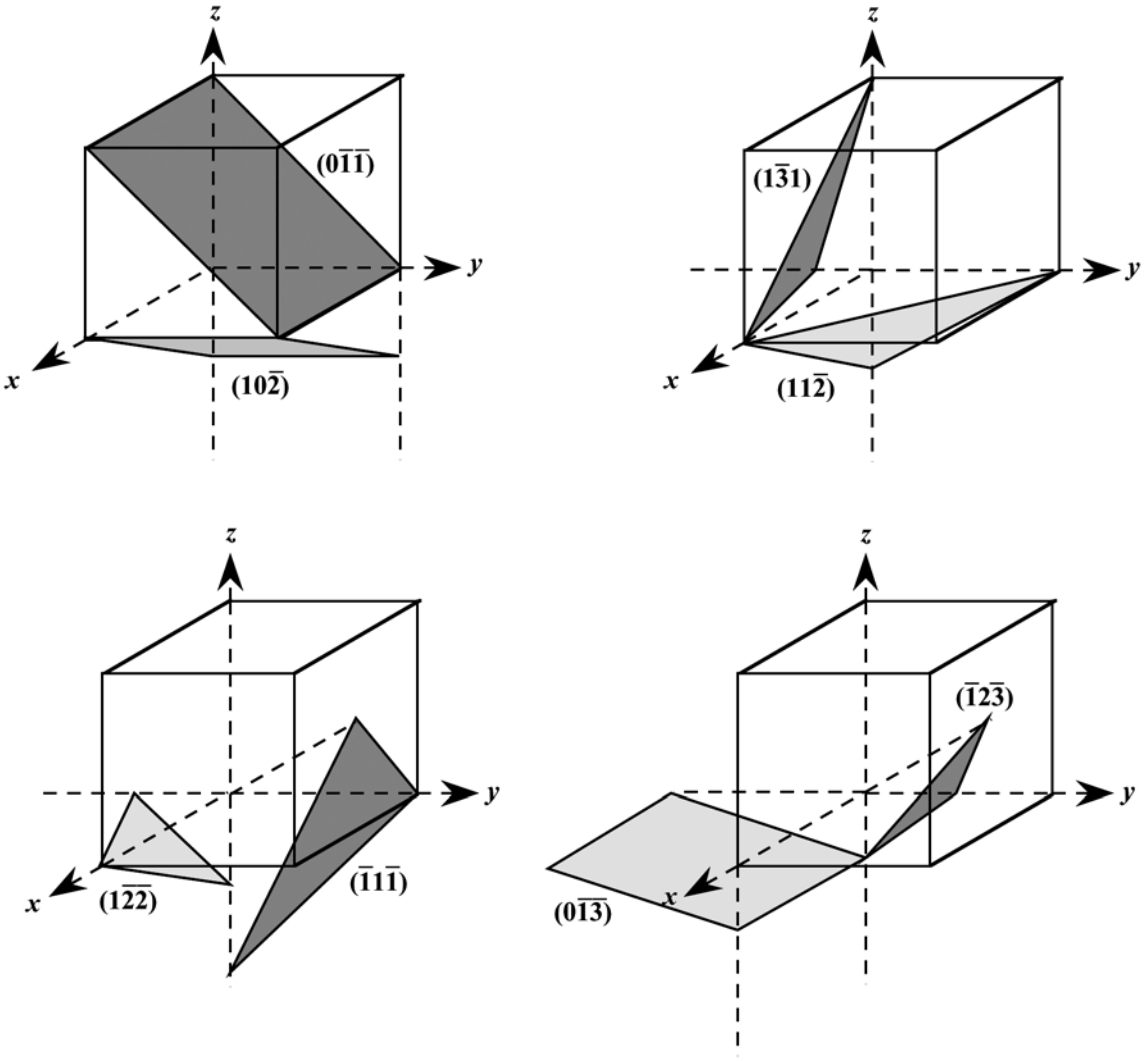
(b) $(11\bar{2})$, *(f)* $(1\bar{2}\bar{2})$,

(c) $(10\bar{2})$, *(g)* $(\bar{1}2\bar{3})$,

(d) $(1\bar{3}1)$, *(h)* $(0\bar{1}\bar{3})$

Solution

The planes called for are plotted in the cubic unit cells shown below.



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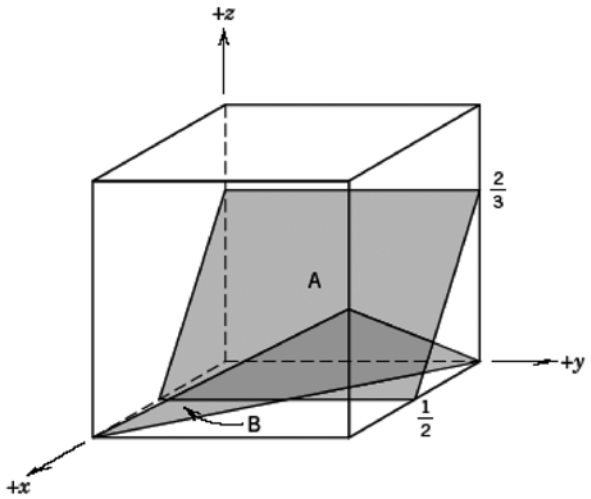
3.41 *Determine the Miller indices for the planes shown in the following unit cell:*



Solution

For plane A we will leave the origin at the unit cell as shown; this is a (403) plane, as summarized below.

	x	y	z
Intercepts	$\frac{a}{2}$	∞b	$\frac{2c}{3}$
Intercepts in terms of a, b, and c	$\frac{1}{2}$	∞	$\frac{2}{3}$
Reciprocals of intercepts	2	0	$\frac{3}{2}$
Reduction	4	0	3
Enclosure		(403)	

For plane B we will move the origin of the unit cell one unit cell distance to the right along the y axis, and one unit cell distance parallel to the x axis; thus, this is a $(\bar{1}\,\bar{1}\,2)$ plane, as summarized below.

	x	y	z
Intercepts	$-a$	$-b$	$\frac{c}{2}$
Intercepts in terms of a, b, and c	-1	-1	$\frac{1}{2}$
Reciprocals of intercepts	-1	-1	2
Reduction		(not necessary)	
Enclosure		$(\bar{1}\,\bar{1}\,2)$	

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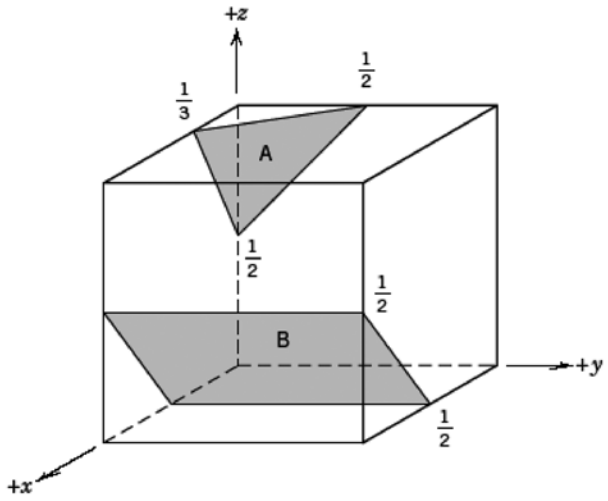
3.42 *Determine the Miller indices for the planes shown in the following unit cell:*



Solution

For plane A we will move the origin of the coordinate system one unit cell distance to the upward along the *z* axis; thus, this is a $(32\bar{2})$ plane, as summarized below.

	x	*y*	*z*
Intercepts	$\frac{a}{3}$	$\frac{b}{2}$	$-\frac{c}{2}$
Intercepts in terms of *a*, *b*, and *c*	$\frac{1}{3}$	$\frac{1}{2}$	$-\frac{1}{2}$
Reciprocals of intercepts	3	2	-2
Reduction		(not necessary)	
Enclosure		$(32\bar{2})$	

For plane B we will move the original of the coordinate system on unit cell distance along the *x* axis; thus, this is a $(\bar{1}01)$ plane, as summarized below.

	x	*y*	*z*
Intercepts	$-\frac{a}{2}$	∞b	$\frac{c}{2}$
Intercepts in terms of *a*, *b*, and *c*	$-\frac{1}{2}$	∞	$\frac{1}{2}$
Reciprocals of intercepts	-2	0	2
Reduction	-1	0	1
Enclosure		$(\bar{1}01)$	

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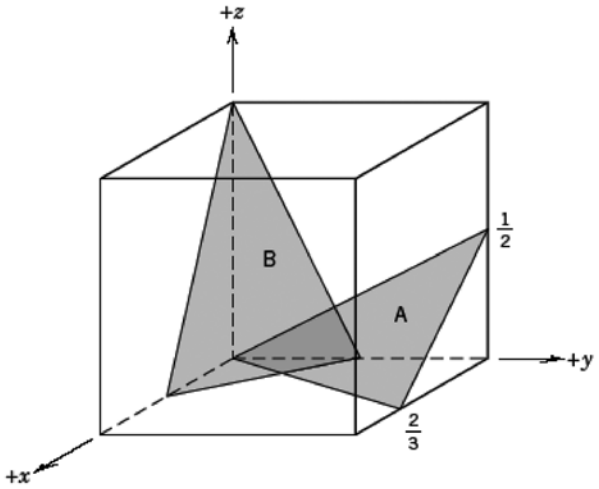
3.43 *Determine the Miller indices for the planes shown in the following unit cell:*



Solution

For plane A since the plane passes through the origin of the coordinate system as shown, we will move the origin of the coordinate system one unit cell distance to the right along the *y* axis; thus, this is a $(3\bar{2}4)$ plane, as summarized below.

	x	*y*	*z*
Intercepts	$\frac{2a}{3}$	$-b$	$\frac{c}{2}$
Intercepts in terms of *a*, *b*, and *c*	$\frac{2}{3}$	-1	$\frac{1}{2}$
Reciprocals of intercepts	$\frac{3}{2}$	-1	2
Reduction	3	-2	4
Enclosure		$(3\bar{2}4)$	

For plane B we will leave the origin at the unit cell as shown; this is a (221) plane, as summarized below.

	x	*y*	*z*
Intercepts	$\frac{a}{2}$	$\frac{b}{2}$	c
Intercepts in terms of *a*, *b*, and *c*	$\frac{1}{2}$	$\frac{1}{2}$	1
Reciprocals of intercepts	2	2	1
Reduction		not necessary	
Enclosure		(221)	

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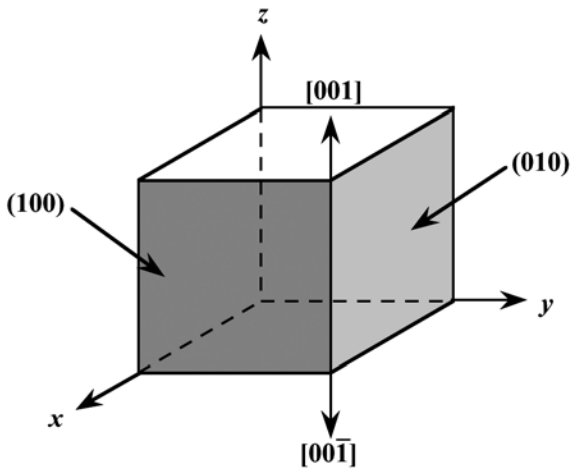
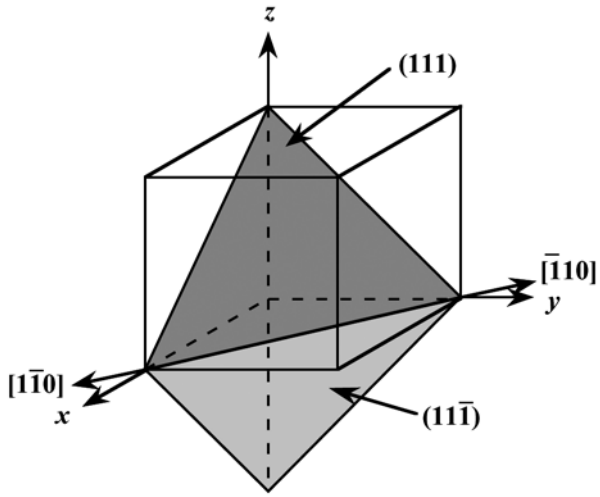
3.44 *Cite the indices of the direction that results from the intersection of each of the following pair of planes within a cubic crystal: (a)* (*100*) *and* (*010*) *planes, (b)* (*111*) *and* ($11\bar{1}$) *planes, and (c)* ($10\bar{1}$) *and* (*001*) *planes.*

Solution

(a) In the figure below is shown (100) and (010) planes, and, as indicated, their intersection results in a [001], or equivalently, a $[00\bar{1}]$ direction.



(b) In the figure below is shown (111) and ($11\bar{1}$) planes, and, as indicated, their intersection results in a $[\bar{1}10]$, or equivalently, a $[1\bar{1}0]$ direction.



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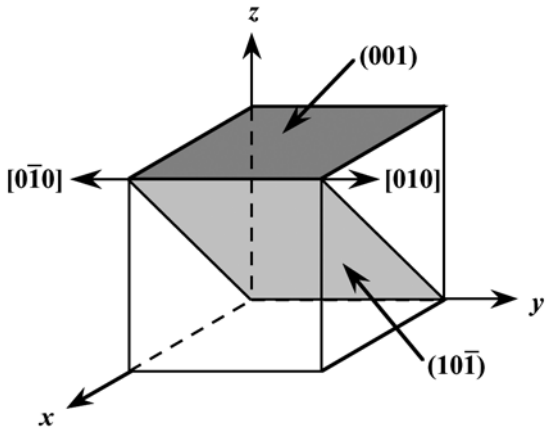
(c) In the figure below is shown $(10\bar{1})$ and (001) planes, and, as indicated, their intersection results in a [010], or equivalently, a $[0\bar{1}0]$ direction.



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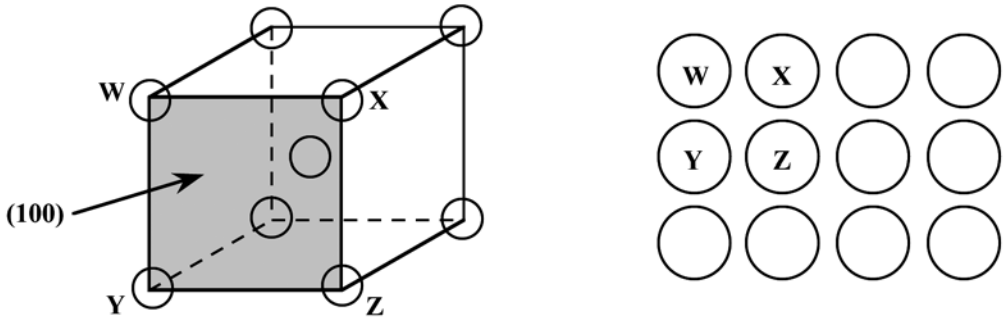
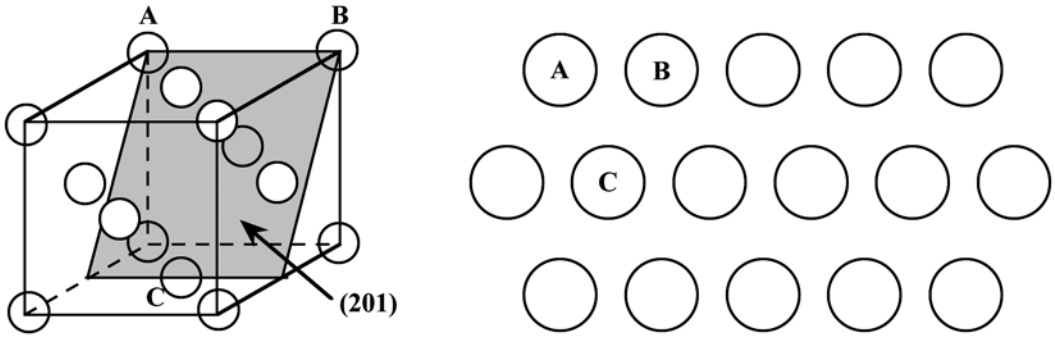
3.45 *Sketch the atomic packing of (a) the (100) plane for the BCC crystal structure, and (b) the (201) plane for the FCC crystal structure (similar to Figures 3.10b and 3.11b).*

Solution

(a) A BCC unit cell, its (100) plane, and the atomic packing of this plane are indicated below. Corresponding atom positions in the two drawings are indicated by letters W, X, Y, and Z.



(b) An FCC unit cell, its (201) plane, and the atomic packing of this plane are indicated below. Corresponding atom positions in the two drawing are indicated by the letters A, B, and C.



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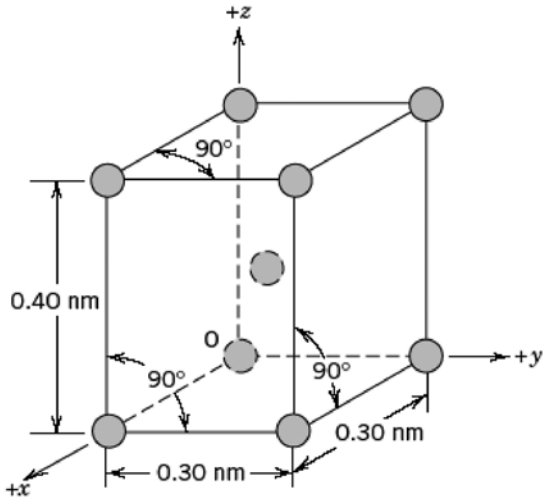
3.46 *Consider the reduced-sphere unit cell shown in Problem 3.20, having an origin of the coordinate system positioned at the atom labeled with an O. For the following sets of planes, determine which are equivalent:*

(a) $(00\bar{1})$, (010), and, $(\bar{1}00)$

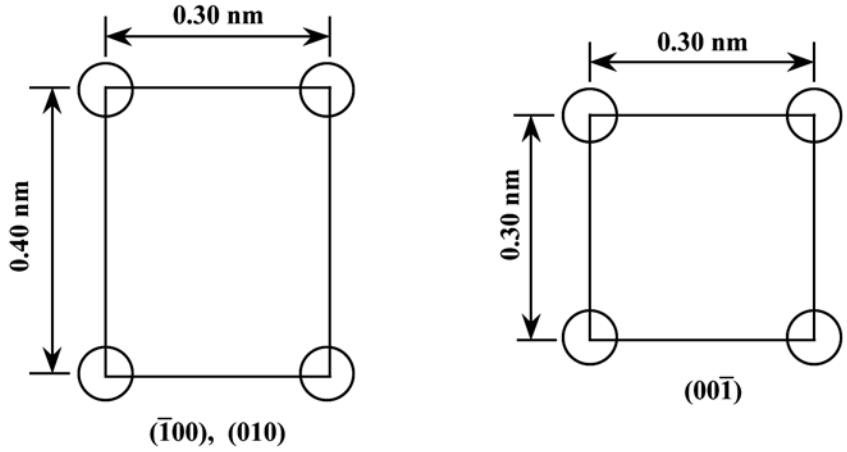
(b) $(1\bar{1}0)$, $(10\bar{1})$, $(0\bar{1}1)$, and $(\bar{1}\bar{1}0)$

(c) $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}1\bar{1})$, $(\bar{1}\bar{1}1)$, and $(1\bar{1}1)$



Solution

(a) The unit cell in Problem 3.20 is body-centered tetragonal. Of the three planes given in the problem statement the $(\bar{1}00)$ and (010) are equivalent—that is, have the same atomic packing. The atomic packing for these two planes as well as the $(00\bar{1})$ are shown in the figure below.



(b) Of the four planes cited in the problem statement, $(1\bar{1}0)$ and $(\bar{1}\bar{1}0)$ are equivalent to one another—have the same atomic packing. The atomic arrangement of these planes is shown in the left drawing below.

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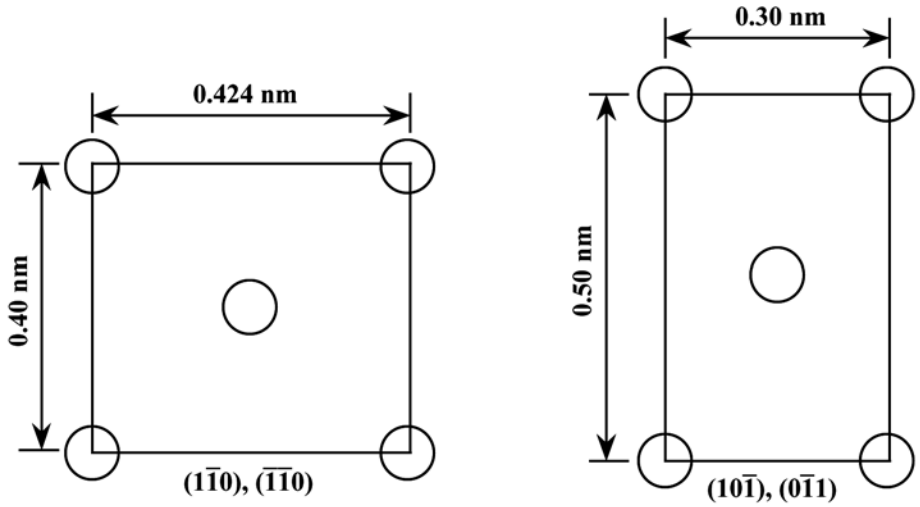
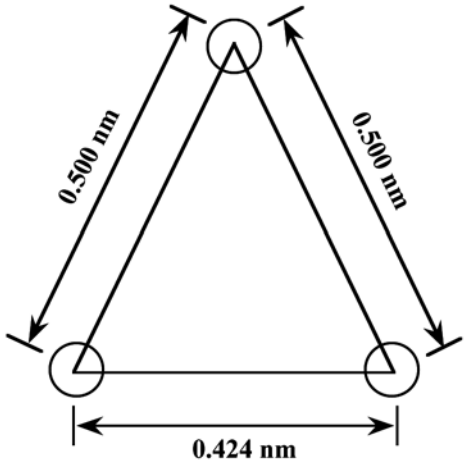
Furthermore, the $(10\bar{1})$ and $(0\bar{1}1)$ are equivalent to each other (but not to the other pair of planes); their atomic arrangement is represented in the other drawing. *Note:* the 0.424 nm dimension in the left-most drawing comes from the relationship $\left[(0.30\text{ nm})^2 + (0.30\text{ nm})^2\right]^{1/2}$. Likewise, the 0.500 nm dimension found in the right-most drawing comes from $\left[(0.30\text{ nm})^2 + (0.40\text{ nm})^2\right]^{1/2}$.



(c) All of the $(\bar{1}\,\bar{1}\,\bar{1})$, $(\bar{1}\,1\,\bar{1})$, $(\bar{1}\,\bar{1}\,1)$, and $(1\,\bar{1}\,1)$ planes are equivalent, that is, have the same atomic packing as illustrated in the following figure:



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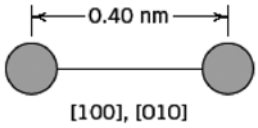
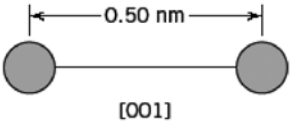
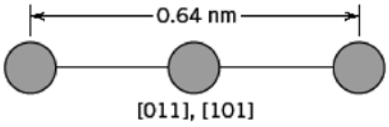
3.47 *Here are shown the atomic packing schemes for several different crystallographic directions for some hypothetical metal. For each direction the circles represent only those atoms contained within a unit cell, which circles are reduced from their actual size.*



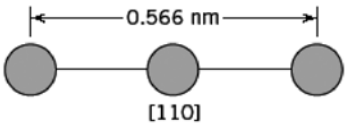
[100], [010]



[001]



[011], [101]



[110]

(a) To what crystal system does the unit cell belong?

(b) What would this crystal structure be called?

Solution

Below is constructed a unit cell using the six crystallographic directions that were provided in the problem.

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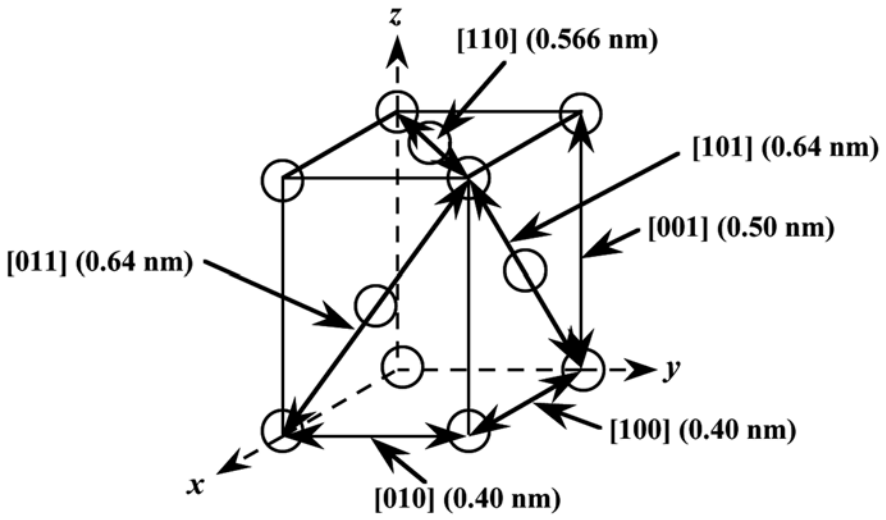

(a) This unit cell belongs to the tetragonal system since $a = b = 0.40$ nm, $c = 0.50$ nm, and $\alpha = \beta = \gamma = 90°$.

(b) This crystal structure would be called *face-centered tetragonal* since the unit cell has tetragonal symmetry, and an atom is located at each of the corners, as well as at the centers of all six unit cell faces. In the figure above, atoms are only shown at the centers of three faces; however, atoms would also be situated at opposite faces.

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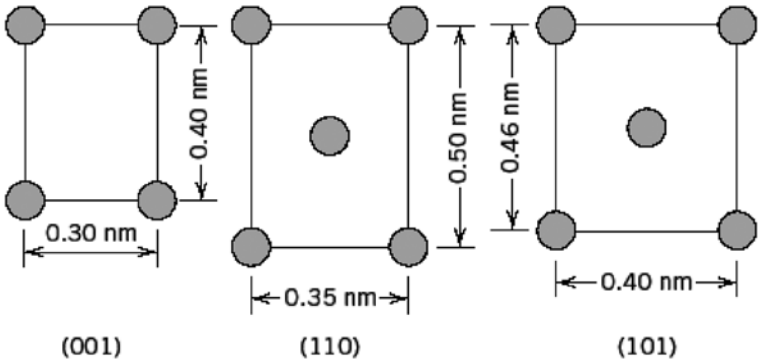
3.48 *Below are shown three different crystallographic planes for a unit cell of some hypothetical metal. The circles represent atoms:*



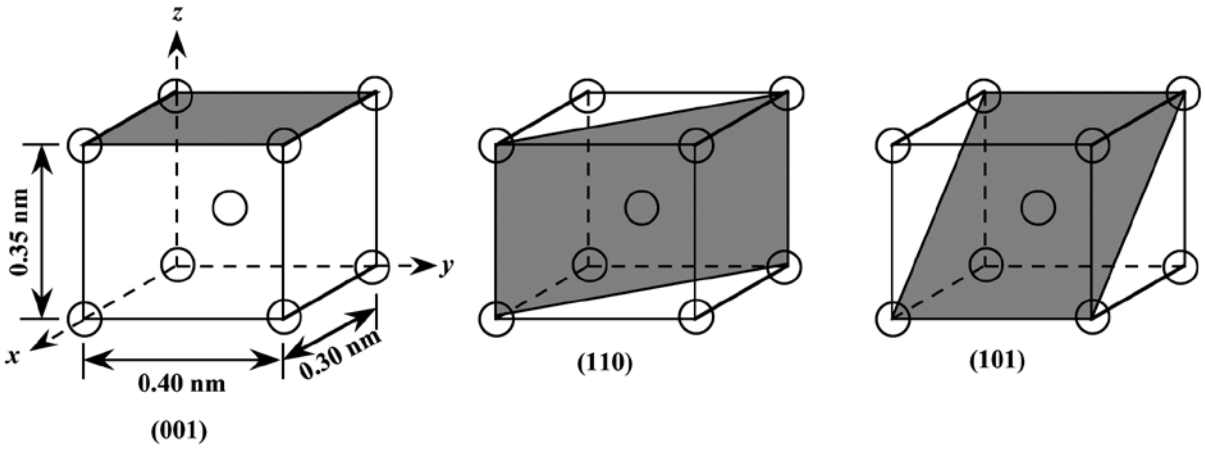
(a) To what crystal system does the unit cell belong?

(b) What would this crystal structure be called?

(c) If the density of this metal is 8.95 g/cm^3, determine its atomic weight.

Solution

The unit cells constructed below show the three crystallographic planes that were provided in the problem statement.



(a) This unit cell belongs to the orthorhombic crystal system since $a = 0.30$ nm, $b = 0.40$ nm, $c = 0.35$ nm, and $\alpha = \beta = \gamma = 90°$.

(b) This crystal structure would be called *body-centered orthorhombic* since the unit cell has orthorhombic symmetry, and an atom is located at each of the corners, as well as at the cell center.

(c) In order to compute its atomic weight, we employ Equation 3.5, with $n = 2$; thus

$$A = \frac{\rho V_C N_A}{n}$$

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$$= \frac{(8.95\ \text{g/cm}^3)\ (3.0)(4.0)(3.5)\ (\times 10^{-24}\ \text{cm}^3\text{/unit cell})(6.022\ \times\ 10^{\ 23}\ \text{atoms/mol})}{2\ \text{atoms/unit cell}}$$

$$= 113.2\ \text{g/mol}$$

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3.49 *Convert the* (*010*) and (*101*) *planes into the four-index Miller–Bravais scheme for hexagonal unit cells.*

Solution

For (010), $h = 0$, $k = 1$, and $l = 0$, and, from Equation 3.7, the value of i is equal to

$$i = -(h + k) = -(0 + 1) = -1$$

Therefore, the (010) plane becomes $(01\bar{1}0)$.

Now for the (101) plane, $h = 1$, $k = 0$, and $l = 1$, and computation of i using Equation 3.7 leads to

$$i = -(h + k) = -[1 + 0] = -1$$

such that (101) becomes $(10\bar{1}1)$.

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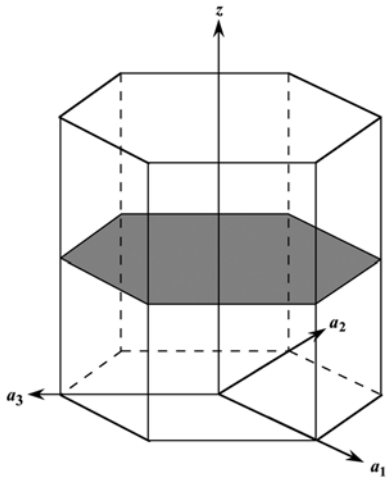
3.50 *Determine the indices for the planes shown in the hexagonal unit cells below:*

Solution



(a)

(a) For this plane, intersections with the a_1, a_2, and z axes are ∞a, ∞a, and $c/2$ (the plane parallels both a_1 and a_2 axes). In terms of a and c these intersections are ∞, ∞, and ½, the respective reciprocals of which are 0, 0, and 2. This means that

$$h = 0$$

$$k = 0$$

$$l = 2$$

Now, from Equation 3.7, the value of i is

$$i = -(h + k) = -[0 + 0] = 0$$

Hence, this is a (0002) plane.

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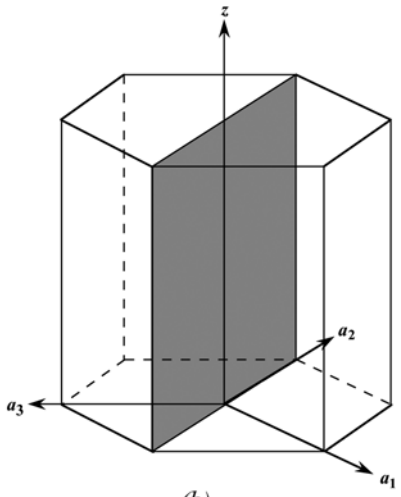
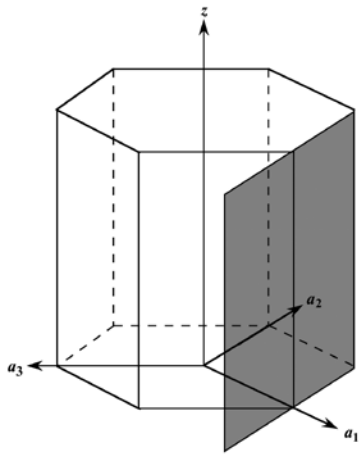


(b)

(b) This plane passes through the origin of the coordinate axis system; therefore, we translate this plane one unit distance along the *x* axis, per the sketch shown below:



At this point the plane intersects the a_1, a_2, and *z* axes at *a*, ∞*a*, and ∞*c*, respectively (the plane parallels both a_2 and *z* axes). In terms of *a* and *c* these intersections are 1, ∞, and ∞, the respective reciprocals of which are 1, 0, and 0. This means that

$$h = 1$$

$$k = 0$$

$$l = 0$$

Now, from Equation 3.7, the value of *i* is

$$i = -(h + k) = -(1 + 0) = -1$$

Hence, this is a $(10\bar{1}0)$ plane.

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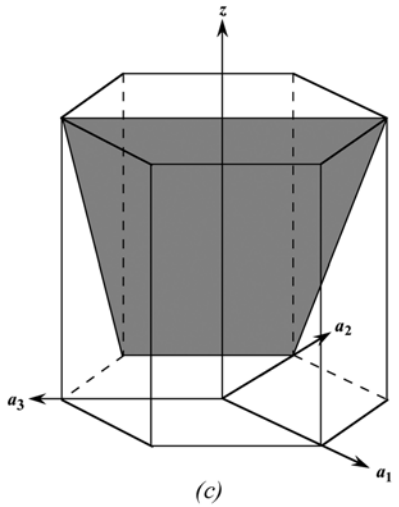


(c)

(c) For this plane, intersections with the a_1, a_2, and z axes are $-a$, a, and c. In terms of a and c these intersections are –1, 1, and 1, the respective reciprocals of which are 0, 1, and 1. This means that

$$h = -1$$

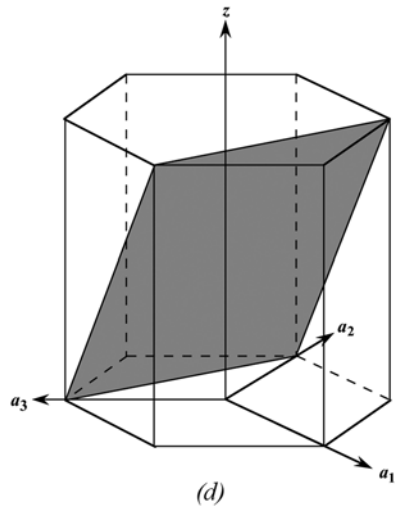
$$k = 1$$

$$l = 1$$

Now, from Equation 3.7, the value of i is

$$i = -(h + k) = -(-1 + 1) = 0$$

Hence, this is a $(\bar{1}101)$ plane.



(d)

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(d) For this plane, intersections with the a_1, a_2, and z axes are $-a/2$, a, and $c/2$, respectively. In terms of a and c these intersections are –1/2, 1, and 1/2, the respective reciprocals of which are –2, 1, and 2. This means that

$$h = -2$$

$$k = 1$$

$$l = 2$$

Now, from Equation 3.7, the value of i is

$$i = -(h + k) = -(-2 + 1) = 1$$

Therefore, this is a $(\bar{2}112)$ plane.

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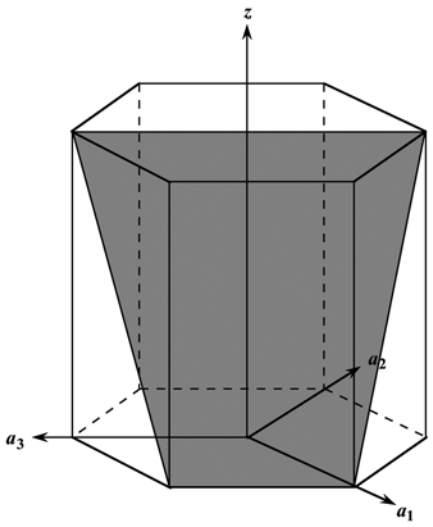
3.51 *Sketch the* $(1\bar{1}01)$ *and* $(11\bar{2}0)$ *planes in a hexagonal unit cell.*

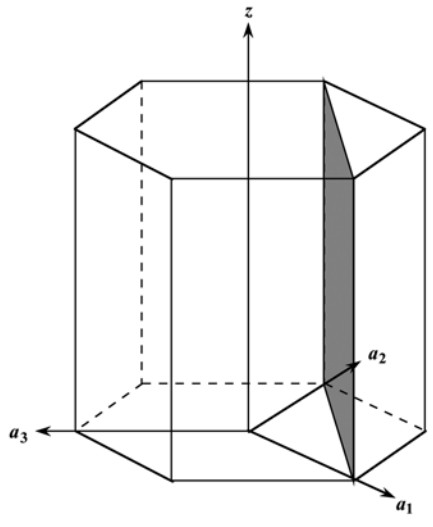
Solution

For $(1\bar{1}01)$ the reciprocals of h, k, i, and l are, respectively, 1, –1, ∞, and 1; thus, this plane is parallel to the a_3 axis, and intersects the a_1 axis at a, the a_2 axis at $-a$, and the z-axis at c. The plane having these intersections is shown in the figure below



$(1\bar{1}01)$

For $(11\bar{2}0)$ the reciprocals of h, k, i, and l are, respectively, 1, 1, –1/2, and ∞; thus, this plane is parallel to the z axis, and intersects the a_1 axis at a, the a_2 axis at a, and the a_3 axis at $-a/2$. The plane having these intersections is shown in the figure below.



$(11\bar{2}0)$

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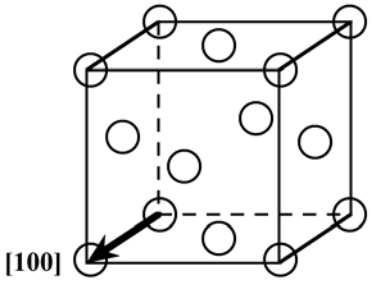
Linear and Planar Densities

3.52 *(a) Derive linear density expressions for FCC [100] and [111] directions in terms of the atomic radius R.*

(b) Compute and compare linear density values for these same two directions for silver.

Solution

(a) In the figure below is shown a [100] direction within an FCC unit cell.

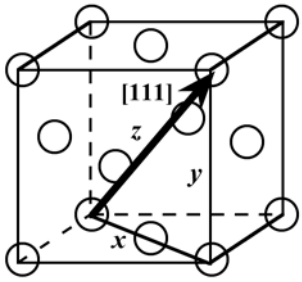


For this [100] direction there is one atom at each of the two unit cell corners, and, thus, there is the equivalent of 1 atom that is centered on the direction vector. The length of this direction vector is just the unit cell edge length, $2R\sqrt{2}$ (Equation 3.1). Therefore, the expression for the linear density of this plane is

$$LD_{100} = \frac{\text{number of atoms centered on [100] direction vector}}{\text{length of [100] direction vector}}$$

$$= \frac{1 \text{ atom}}{2R\sqrt{2}} = \frac{1}{2R\sqrt{2}}$$

An FCC unit cell within which is drawn a [111] direction is shown below.



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For this [111] direction, the vector shown passes through only the centers of the single atom at each of its ends, and, thus, there is the equivalence of 1 atom that is centered on the direction vector. The length of this direction vector is denoted by z in this figure, which is equal to

$$z = \sqrt{x^2 + y^2}$$

where x is the length of the bottom face diagonal, which is equal to $4R$. Furthermore, y is the unit cell edge length, which is equal to $2R\sqrt{2}$ (Equation 3.1). Thus, using the above equation, the length z may be calculated as follows:

$$z = \sqrt{(4R)^2 + (2R\sqrt{2})^2} = \sqrt{24R^2} = 2R\sqrt{6}$$

Therefore, the expression for the linear density of this direction is

$$\text{LD}_{111} = \frac{\text{number of atoms centered on [111] direction vector}}{\text{length of [111] direction vector}}$$

$$= \frac{1 \text{ atom}}{2R\sqrt{6}} = \frac{1}{2R\sqrt{6}}$$

(b) From the table inside the front cover, the atomic radius for silver is 0.144 nm. Therefore, the linear density for the [100] direction is

$$\text{LD}_{100}(\text{Ag}) = \frac{1}{2R\sqrt{2}} = \frac{1}{(2)(0.144 \text{ nm})\sqrt{2}} = 2.46 \text{ nm}^{-1} = 2.46 \times 10^9 \text{ m}^{-1}$$

While for the [111] direction

$$\text{LD}_{111}(\text{Ag}) = \frac{1}{2R\sqrt{6}} = \frac{1}{(2)(0.144 \text{ nm})\sqrt{6}} = 1.42 \text{ nm}^{-1} = 1.42 \times 10^9 \text{ m}^{-1}$$

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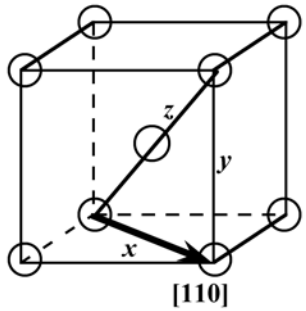
3.53 *(a) Derive linear density expressions for BCC* [*110*] *and* [*111*] *directions in terms of the atomic radius R.*

(b) Compute and compare linear density values for these same two directions for tungsten.

Solution

(a) In the figure below is shown a [110] direction within a BCC unit cell.



For this [110] direction there is one atom at each of the two unit cell corners, and, thus, there is the equivalence of 1 atom that is centered on the direction vector. The length of this direction vector is denoted by x in this figure, which is equal to

$$x = \sqrt{z^2 - y^2}$$

where y is the unit cell edge length, which, from Equation 3.3 is equal to $\frac{4R}{\sqrt{3}}$. Furthermore, z is the length of the unit cell diagonal, which is equal to $4R$ Thus, using the above equation, the length x may be calculated as follows:

$$x = \sqrt{(4R)^2 - \left(\frac{4R}{\sqrt{3}}\right)^2} = \sqrt{\frac{32R^2}{3}} = 4R\sqrt{\frac{2}{3}}$$

Therefore, the expression for the linear density of this direction is

$$\mathrm{LD}_{110} = \frac{\text{number of atoms centered on [110] direction vector}}{\text{length of [110] direction vector}}$$

$$= \frac{1 \text{ atom}}{4R\sqrt{\frac{2}{3}}} = \frac{\sqrt{3}}{4R\sqrt{2}}$$

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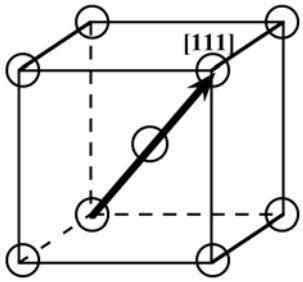
A BCC unit cell within which is drawn a [111] direction is shown below.



For although the [111] direction vector shown passes through the centers of three atoms, there is an equivalence of only two atoms associated with this unit cell—one-half of each of the two atoms at the end of the vector, in addition to the center atom belongs entirely to the unit cell. Furthermore, the length of the vector shown is equal to $4R$, since all of the atoms whose centers the vector passes through touch one another. Therefore, the linear density is equal to

$$\text{LD}_{111} = \frac{\text{number of atoms centered on [111] direction vector}}{\text{length of [111] direction vector}}$$

$$= \frac{2 \text{ atoms}}{4R} = \frac{1}{2R}$$

(b) From the table inside the front cover, the atomic radius for tungsten is 0.137 nm. Therefore, the linear density for the [110] direction is

$$\text{LD}_{110}(\text{W}) = \frac{\sqrt{3}}{4R\sqrt{2}} = \frac{\sqrt{3}}{(4)(0.137 \text{ nm})\sqrt{2}} = 2.23 \text{ nm}^{-1} = 2.23 \times 10^9 \text{ m}^{-1}$$

While for the [111] direction

$$\text{LD}_{111}(\text{W}) = \frac{1}{2R} = \frac{1}{(2)(0.137 \text{ nm})} = 3.65 \text{ nm}^{-1} = 3.65 \times 10^9 \text{ m}^{-1}$$

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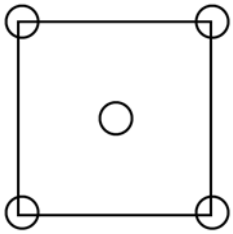
3.54 *(a) Derive planar density expressions for FCC (100) and (111) planes in terms of the atomic radius R.*

(b) Compute and compare planar density values for these same two planes for nickel.

Solution

(a) In the figure below is shown a (100) plane for an FCC unit cell.

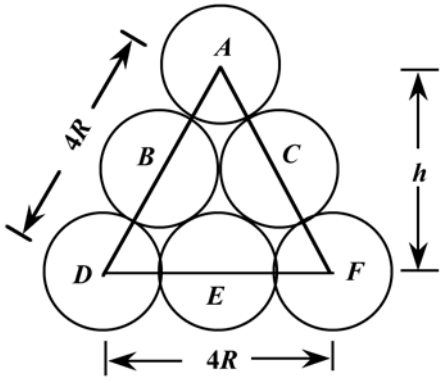


For this (100) plane there is one atom at each of the four cube corners, each of which is shared with four adjacent unit cells, while the center atom lies entirely within the unit cell. Thus, there is the equivalence of 2 atoms associated with this FCC (100) plane. The planar section represented in the above figure is a square, wherein the side lengths are equal to the unit cell edge length, $2R\sqrt{2}$ (Equation 3.1); and, thus, the area of this square is just $(2R\sqrt{2})^2 = 8R^2$. Hence, the planar density for this (100) plane is just

$$\text{PD}_{100} = \frac{\text{number of atoms centered on (100) plane}}{\text{area of (100) plane}}$$

$$= \frac{2 \text{ atoms}}{8R^2} = \frac{1}{4R^2}$$

That portion of an FCC (111) plane contained within a unit cell is shown below.



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There are six atoms whose centers lie on this plane, which are labeled *A* through *F*. One-sixth of each of atoms *A*, *D*, and *F* are associated with this plane (yielding an equivalence of one-half atom), with one-half of each of atoms *B*, *C*, and *E* (or an equivalence of one and one-half atoms) for a total equivalence of two atoms. Now, the area of the triangle shown in the above figure is equal to one-half of the product of the base length and the height, *h*. If we consider half of the triangle, then

$$(2R)^2 + h^2 = (4R)^2$$

which leads to $h = 2R\sqrt{3}$. Thus, the area is equal to

$$\text{Area} = \frac{4R(h)}{2} = \frac{(4R)\left(2R\sqrt{3}\right)}{2} = 4R^2\sqrt{3}$$

And, thus, the planar density is

$$\text{PD}_{111} = \frac{\text{number of atoms centered on (111) plane}}{\text{area of (111) plane}}$$

$$= \frac{2 \text{ atoms}}{4R^2\sqrt{3}} = \frac{1}{2R^2\sqrt{3}}$$

(b) From the table inside the front cover, the atomic radius for nickel is 0.125 nm. Therefore, the planar density for the (100) plane is

$$\text{PD}_{100}(\text{Ni}) = \frac{1}{4R^2} = \frac{1}{4\,(0.125 \text{ nm})^2} = 16.00 \text{ nm}^{-2} = 1.600 \times 10^{19} \text{ m}^{-2}$$

While for the (111) plane

$$\text{PD}_{111}(\text{Ni}) = \frac{1}{2R^2\sqrt{3}} = \frac{1}{2\sqrt{3}\,(0.125 \text{ nm})^2} = 18.48 \text{ nm}^{-2} = 1.848 \times 10^{19} \text{ m}^{-2}$$

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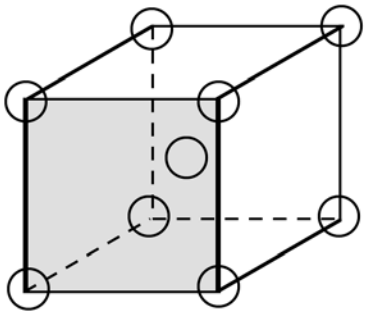
3.55 *(a) Derive planar density expressions for BCC (100) and (110) planes in terms of the atomic radius R.*

(b) Compute and compare planar density values for these same two planes for vanadium.

Solution

(a) A BCC unit cell within which is drawn a (100) plane is shown below.



For this (100) plane there is one atom at each of the four cube corners, each of which is shared with four adjacent unit cells. Thus, there is the equivalence of 1 atom associated with this BCC (100) plane. The planar section represented in the above figure is a square, wherein the side lengths are equal to the unit cell edge length, $\frac{4R}{\sqrt{3}}$ (Equation 3.3); and, thus, the area of this square is just $\left(\frac{4R}{\sqrt{3}}\right)^2 = \frac{16R^2}{3}$. Hence, the planar density for this (100) plane is just

$$PD_{100} = \frac{\text{number of atoms centered on (100) plane}}{\text{area of (100) plane}}$$

$$= \frac{1 \text{ atom}}{\frac{16R^2}{3}} = \frac{3}{16R^2}$$

A BCC unit cell within which is drawn a (110) plane is shown below.

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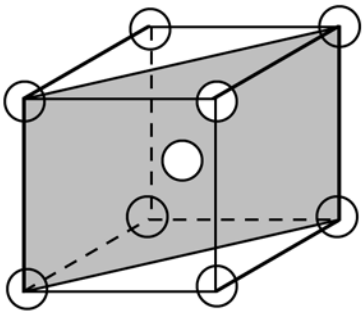
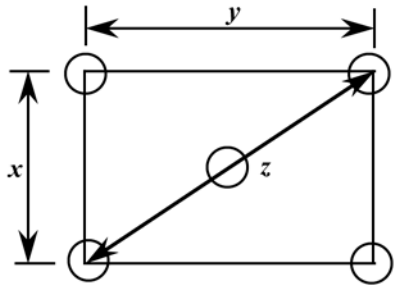


For this (110) plane there is one atom at each of the four cube corners through which it passes, each of which is shared with four adjacent unit cells, while the center atom lies entirely within the unit cell. Thus, there is the equivalence of 2 atoms associated with this BCC (110) plane. The planar section represented in the above figure is a rectangle, as noted in the figure below.



From this figure, the area of the rectangle is the product of x and y. The length x is just the unit cell edge length, which for BCC (Equation 3.3) is $\frac{4R}{\sqrt{3}}$. Now, the diagonal length z is equal to $4R$. For the triangle bounded by the lengths x, y, and z

$$y = \sqrt{z^2 - x^2}$$

Or

$$y = \sqrt{(4R)^2 - \left(\frac{4R}{\sqrt{3}}\right)^2} = \frac{4R\sqrt{2}}{\sqrt{3}}$$

Thus, in terms of R, the area of this (110) plane is just

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$$\text{Area}(110) = xy = \left(\frac{4R}{\sqrt{3}}\right)\left(\frac{4R\sqrt{2}}{\sqrt{3}}\right) = \frac{16R^2\sqrt{2}}{3}$$

And, finally, the planar density for this (110) plane is just

$$\text{PD}_{110} = \frac{\text{number of atoms centered on (110) plane}}{\text{area of (110) plane}}$$

$$= \frac{2 \text{ atoms}}{\frac{16R^2\sqrt{2}}{3}} = \frac{3}{8R^2\sqrt{2}}$$

(b) From the table inside the front cover, the atomic radius for vanadium is 0.132 nm. Therefore, the planar density for the (100) plane is

$$\text{PD}_{100}(\text{V}) = \frac{3}{16R^2} = \frac{3}{16(0.132 \text{ nm})^2} = 10.76 \text{ nm}^{-2} = 1.076 \times 10^{19} \text{ m}^{-2}$$

While for the (110) plane

$$\text{PD}_{110}(\text{V}) = \frac{3}{8R^2\sqrt{2}} = \frac{3}{8(0.132 \text{ nm})^2\sqrt{2}} = 15.22 \text{ nm}^{-2} = 1.522 \times 10^{19} \text{ m}^{-2}$$

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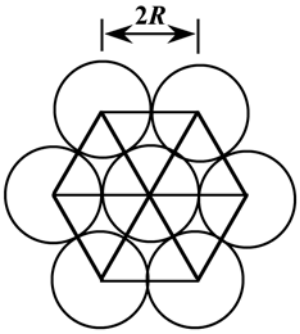
3.56 *(a) Derive the planar density expression for the HCP (0001) plane in terms of the atomic radius R.*

(b) Compute the planar density value for this same plane for magnesium.

Solution

(a) A (0001) plane for an HCP unit cell is show below.



Each of the 6 perimeter atoms in this plane is shared with three other unit cells, whereas the center atom is shared with no other unit cells; this gives rise to three equivalent atoms belonging to this plane.

In terms of the atomic radius R, the area of each of the 6 equilateral triangles that have been drawn is $R^2\sqrt{3}$, or the total area of the plane shown is $6R^2\sqrt{3}$. And the planar density for this (0001) plane is equal to

$$\text{PD}_{0001} = \frac{\text{number of atoms centered on (0001) plane}}{\text{area of (0001) plane}}$$

$$= \frac{3 \text{ atoms}}{6R^2\sqrt{3}} = \frac{1}{2R^2\sqrt{3}}$$

(b) From the table inside the front cover, the atomic radius for magnesium is 0.160 nm. Therefore, the planar density for the (0001) plane is

$$\text{PD}_{0001}(\text{Mg}) = \frac{1}{2R^2\sqrt{3}} = \frac{1}{2(0.160 \text{ nm})^2\sqrt{3}} = 11.28 \text{ nm}^{-2} = 1.128 \times 10^{19} \text{ m}^{-2}$$

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Polycrystalline Materials

3.57 *Explain why the properties of polycrystalline materials are most often isotropic.*

Solution

Although each individual grain in a polycrystalline material may be anisotropic, if the grains have random orientations, then the solid aggregate of the many anisotropic grains will behave isotropically.

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X-ray Diffraction: Determination of Crystal Structures

3.58 *Using the data for molybdenum in Table 3.1, compute the interplanar spacing for the* (*111*) *set of planes.*

Solution

From the Table 3.1, molybdenum has a BCC crystal structure and an atomic radius of 0.1363 nm. Using Equation (3.3), the lattice parameter a may be computed as

$$a = \frac{4R}{\sqrt{3}} = \frac{(4)(0.1363\ \text{nm})}{\sqrt{3}} = 0.3148\ \text{nm}$$

Now, the interplanar spacing d_{111} maybe determined using Equation 3.14 as

$$d_{111} = \frac{a}{\sqrt{(1)^2 + (1)^2 + (1)^2}} = \frac{0.3148\ \text{nm}}{\sqrt{3}} = 0.1817\ \text{nm}$$

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3.59 *Determine the expected diffraction angle for the first-order reflection from the* (*113*) *set of planes for FCC platinum when monochromatic radiation of wavelength 0.1542 nm is used.*

Solution

We first calculate the lattice parameter using Equation 3.1 and the value of R (0.1387 nm) cited in Table 3.1, as follows:

$$a = 2R\sqrt{2} = (2)(0.1387 \text{ nm})(\sqrt{2}) = 0.3923 \text{ nm}$$

Next, the interplanar spacing for the (113) set of planes may be determined using Equation 3.14 according to

$$d_{113} = \frac{a}{\sqrt{(1)^2 + (1)^2 + (3)^2}} = \frac{0.3923 \text{ nm}}{\sqrt{11}} = 0.1183 \text{ nm}$$

And finally, employment of Equation 3.13 yields the diffraction angle as

$$\sin\theta = \frac{n\lambda}{2d_{113}} = \frac{(1)(0.1542 \text{ nm})}{(2)(0.1183 \text{ nm})} = 0.652$$

Which leads to

$$\theta = \sin^{-1}(0.652) = 40.69°$$

And, finally

$$2\theta = (2)(40.69°) = 81.38°$$

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3.60 *Using the data for aluminum in Table 3.1, compute the interplanar spacings for the* (*110*) *and* (*221*) *sets of planes.*

Solution

From the table, aluminum has an FCC crystal structure and an atomic radius of 0.1431 nm. Using Equation 3.1 the lattice parameter, a, may be computed as

$$a = 2R\sqrt{2} = (2)(0.1431 \text{ nm})(\sqrt{2}) = 0.4047 \text{ nm}$$

Now, the d_{110} interplanar spacing may be determined using Equation 3.14 as

$$d_{110} = \frac{a}{\sqrt{(1)^2 + (1)^2 + (0)^2}} = \frac{0.4047 \text{ nm}}{\sqrt{2}} = 0.2862 \text{ nm}$$

And, similarly for d_{221}

$$d_{221} = \frac{a}{\sqrt{(2)^2 + (2)^2 + (1)^2}} = \frac{0.4047 \text{ nm}}{\sqrt{9}} = 0.1349 \text{ nm}$$

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3.61 *The metal iridium has an FCC crystal structure. If the angle of diffraction for the* (*220*) *set of planes occurs at 69.22° (first-order reflection) when monochromatic x-radiation having a wavelength of 0.1542 nm is used, compute (a) the interplanar spacing for this set of planes, and (b) the atomic radius for an iridium atom.*

Solution

(a) From the data given in the problem, and realizing that 69.22° = 2θ, the interplanar spacing for the (220) set of planes for iridium may be computed using Equation 3.13 as

$$d_{220} = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(0.1542 \text{ nm})}{(2)\left(\sin \frac{69.22°}{2}\right)} = 0.1357 \text{ nm}$$

(b) In order to compute the atomic radius we must first determine the lattice parameter, *a*, using Equation 3.14, and then *R* from Equation 3.1 since Ir has an FCC crystal structure. Therefore,

$$a = d_{220}\sqrt{(2)^2 + (2)^2 + (0)^2} = (0.1357 \text{ nm})\left(\sqrt{8}\right) = 0.3838 \text{ nm}$$

And, from Equation 3.1

$$R = \frac{a}{2\sqrt{2}} = \frac{0.3838 \text{ nm}}{2\sqrt{2}} = 0.1357 \text{ nm}$$

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3.62 *The metal rubidium has a BCC crystal structure. If the angle of diffraction for the* (*321*) *set of planes occurs at 27.00° (first-order reflection) when monochromatic x-radiation having a wavelength of 0.0711 nm is used, compute (a) the interplanar spacing for this set of planes, and (b) the atomic radius for the rubidium atom.*

Solution

(a) From the data given in the problem, and realizing that 27.00° = 2θ, the interplanar spacing for the (321) set of planes for Rb may be computed using Equation 3.13 as follows:

$$d_{321} = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(0.0711 \text{ nm})}{(2)\left(\sin \frac{27.00°}{2}\right)} = 0.1523 \text{ nm}$$

(b) In order to compute the atomic radius we must first determine the lattice parameter, *a*, using Equation 3.14, and then *R* from Equation 3.3 since Rb has a BCC crystal structure. Therefore,

$$a = d_{321}\sqrt{(3)^2 + (2)^2 + (1)^2} = (0.1523 \text{ nm})\left(\sqrt{14}\right) = 0.5700 \text{ nm}$$

And, from Equation 3.3

$$R = \frac{a\sqrt{3}}{4} = \frac{(0.5700 \text{ nm})\sqrt{3}}{4} = 0.2468 \text{ nm}$$

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3.63 *For which set of crystallographic planes will a first-order diffraction peak occur at a diffraction angle of 46.21° for BCC iron when monochromatic radiation having a wavelength of 0.0711 nm is used?*

Solution

The first step to solve this problem is to compute the interplanar spacing using Equation 3.13. Thus,

$$d_{hkl} = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(0.0711 \text{ nm})}{(2)\left(\sin \frac{46.21°}{2}\right)} = 0.0906 \text{ nm}$$

Now, employment of both Equations 3.14 and 3.3 (since Fe's crystal structure is BCC), and the value of R for iron from Table 3.1 (0.1241 nm) leads to

$$\sqrt{h^2 + k^2 + l^2} = \frac{a}{d_{hkl}} = \frac{4R}{d_{hkl}\sqrt{3}}$$

$$= \frac{(4)(0.1241 \text{ nm})}{(0.0906 \text{ nm})(\sqrt{3})} = 3.163$$

This means that

$$h^2 + k^2 + l^2 = (3.163)^2 = 10.0$$

By trial and error, the only three integers having a sum that is even, and the sum of the squares of which equals 10.0 are 3, 1, and 0. Therefore, the set of planes responsible for this diffraction peak are the (310) ones.

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3.64 *Figure 3.22 shows an x-ray diffraction pattern for α-iron taken using a diffractometer and monochromatic x-radiation having a wavelength of 0.1542 nm; each diffraction peak on the pattern has been indexed. Compute the interplanar spacing for each set of planes indexed; also determine the lattice parameter of Fe for each of the peaks.*

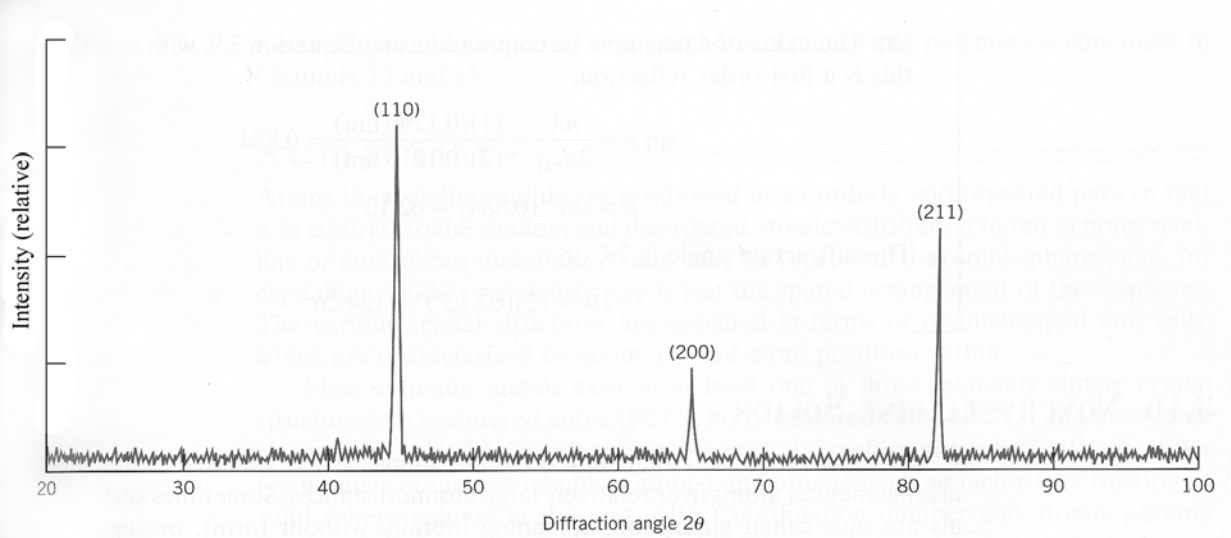

FIGURE 3.22 Diffraction pattern for polycrystalline α-iron.

Solution

For each peak, in order to compute the interplanar spacing and the lattice parameter we must employ Equations 3.14 and 3.13, respectively. The first peak of Figure 3.22, which results from diffraction by the (110) set of planes, occurs at $2\theta = 45.0°$; the corresponding interplanar spacing for this set of planes, using Equation 3.13, is equal to

$$d_{110} = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(0.1542 \text{ nm})}{(2)\left(\sin \frac{45.0°}{2}\right)} = 0.2015 \text{ nm}$$

And, from Equation 3.14, the lattice parameter a is determined as

$$a = d_{hkl}\sqrt{(h)^2 + (k)^2 + (l)^2} = d_{110}\sqrt{(1)^2 + (1)^2 + (0)^2}$$

$$= (0.2015 \text{ nm})\sqrt{2} = 0.2850 \text{ nm}$$

Similar computations are made for the other peaks which results are tabulated below:

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Peak Index	2θ	d_{hkl}(nm)	a (nm)
200	65.1	0.1433	0.2866
211	82.8	0.1166	0.2856

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3.65 *The diffraction peaks shown in Figure 3.22 are indexed according to the reflection rules for BCC (i.e., the sum h + k + l must be even). Cite the h, k, and l indices for the first four diffraction peaks for FCC crystals consistent with h, k, and l all being either odd or even.*

Solution

The first four diffraction peaks that will occur for FCC consistent with *h*, *k*, and *l* all being odd or even are (111), (200), (220), and (311).

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3.66 *Figure 3.25 shows the first four peaks of the x-ray diffraction pattern for copper, which has an FCC crystal structure; monochromatic x-radiation having a wavelength of 0.1542 nm was used.*

(a) Index (i.e., give h, k, and l indices) for each of these peaks.

(b) Determine the interplanar spacing for each of the peaks.

(c) For each peak, determine the atomic radius for Cu and compare these with the value presented in Table 3.1.

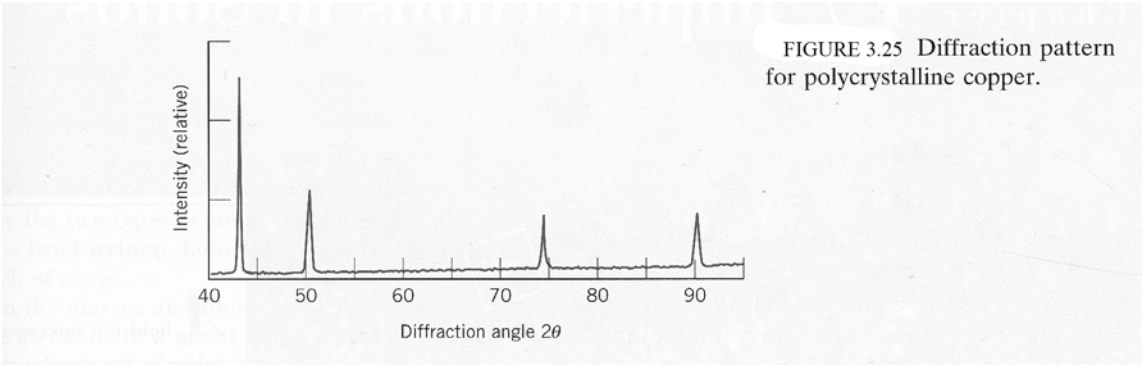

FIGURE 3.25 Diffraction pattern for polycrystalline copper.

Solution

(a) Since Cu has an FCC crystal structure, only those peaks for which *h*, *k*, and *l* are all either odd or even will appear. Therefore, the first peak results by diffraction from (111) planes.

(b) For each peak, in order to calculate the interplanar spacing we must employ Equation 3.13. For the first peak which occurs at 43.8°

$$d_{111} = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(0.1542 \text{ nm})}{(2)\left(\sin \frac{43.8°}{2}\right)} = 0.2067 \text{ nm}$$

(c) Employment of Equations 3.14 and 3.1 is necessary for the computation of *R* for Cu as

$$R = \frac{a}{2\sqrt{2}} = \frac{(d_{hkl})\sqrt{(h)^2 + (k)^2 + (l)^2}}{2\sqrt{2}}$$

$$= \frac{(0.2067 \text{ nm})\sqrt{(1)^2 + (1)^2 + (1)^2}}{2\sqrt{2}}$$

$$= 0.1266 \text{ nm}$$

Similar computations are made for the other peaks which results are tabulated below:

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Peak Index	2θ	d_{hkl}(nm)	R (nm)
200	50.8	0.1797	0.1271
220	74.4	0.1275	0.1275
311	90.4	0.1087	0.1274

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Noncrystalline Solids

3.67 *Would you expect a material in which the atomic bonding is predominantly ionic in nature to be more or less likely to form a noncrystalline solid upon solidification than a covalent material? Why? (See Section 2.6.)*

Solution

A material in which atomic bonding is predominantly ionic in nature is less likely to form a noncrystalline solid upon solidification than a covalent material because covalent bonds are directional whereas ionic bonds are nondirectional; it is more difficult for the atoms in a covalent material to assume positions giving rise to an ordered structure.

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CHAPTER 4

IMPERFECTIONS IN SOLIDS

PROBLEM SOLUTIONS

Vacancies and Self-Interstitials

4.1 *Calculate the fraction of atom sites that are vacant for lead at its melting temperature of 327°C (600 K). Assume an energy for vacancy formation of 0.55 eV/atom.*

Solution

In order to compute the fraction of atom sites that are vacant in lead at 600 K, we must employ Equation 4.1. As stated in the problem, Q_v = 0.55 eV/atom. Thus,

$$\frac{N_v}{N} = \exp\left(-\frac{Q_v}{kT}\right) = \exp\left[-\frac{0.55 \text{ eV/atom}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(600 \text{ K})}\right]$$

$$= 2.41 \times 10^{-5}$$

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4.2 *Calculate the number of vacancies per cubic meter in iron at 850°C. The energy for vacancy formation is 1.08 eV/atom. Furthermore, the density and atomic weight for Fe are 7.65 g/cm^3 and 55.85 g/mol, respectively.*

Solution

Determination of the number of vacancies per cubic meter in iron at 850°C (1123 K) requires the utilization of Equations 4.1 and 4.2 as follows:

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right) = \frac{N_A \rho_{Fe}}{A_{Fe}} \exp\left(-\frac{Q_v}{kT}\right)$$

And incorporation of values of the parameters provided in the problem statement into the above equation leads to

$$N_v = \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(7.65\ \text{g/cm}^3)}{55.85\ \text{g/mol}} \exp\left[-\frac{1.08\ \text{eV/atom}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(850°\text{C} + 273\ \text{K})}\right]$$

$$= 1.18 \times 10^{18}\ \text{cm}^{-3} = 1.18 \times 10^{24}\ \text{m}^{-3}$$

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4.3 *Calculate the activation energy for vacancy formation in aluminum, given that the equilibrium number of vacancies at 500°C (773 K) is 7.57×10^{23} m^{-3}. The atomic weight and density (at 500°C) for aluminum are, respectively, 26.98 g/mol and 2.62 g/cm^3.*

Solution

Upon examination of Equation 4.1, all parameters besides Q_v are given except N, the total number of atomic sites. However, N is related to the density, (ρ_{Al}), Avogadro's number (N_A), and the atomic weight (A_{Al}) according to Equation 4.2 as

$$N = \frac{N_A \rho_{Al}}{A_{Al}}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(2.62 \text{ g/cm}^3)}{26.98 \text{ g/mol}}$$

$$= 5.85 \times 10^{22} \text{ atoms/cm}^3 = 5.85 \times 10^{28} \text{ atoms/m}^3$$

Now, taking natural logarithms of both sides of Equation 4.1,

$$\ln N_v = \ln N - \frac{Q_v}{kT}$$

and, after some algebraic manipulation

$$Q_v = -kT \ln\left(\frac{N_v}{N}\right)$$

$$= -(8.62 \times 10^{-5} \text{ eV/atom-K})(500°\text{C} + 273 \text{ K}) \ln\left[\frac{7.57 \times 10^{23} \text{ m}^{-3}}{5.85 \times 10^{28} \text{ m}^{-3}}\right]$$

$$= 0.75 \text{ eV/atom}$$

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Impurities in Solids

4.4 *Below, atomic radius, crystal structure, electronegativity, and the most common valence are tabulated, for several elements; for those that are nonmetals, only atomic radii are indicated.*

Element	***Atomic Radius (nm)***	***Crystal Structure***	***Electronegativity***	***Valence***
Cu	0.1278	FCC	1.9	+2
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Ni	0.1246	FCC	1.8	+2
Pd	0.1376	FCC	2.2	+2
Pt	0.1387	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+2

Which of these elements would you expect to form the following with copper:

(a) A substitutional solid solution having complete solubility

(b) A substitutional solid solution of incomplete solubility

(c) An interstitial solid solution

Solution

In this problem we are asked to cite which of the elements listed form with Cu the three possible solid solution types. For complete substitutional solubility the following criteria must be met: 1) the difference in atomic radii between Cu and the other element ($\Delta R\%$) must be less than ±15%, 2) the crystal structures must be the same, 3) the electronegativities must be similar, and 4) the valences should be the same, or nearly the same. Below are tabulated, for the various elements, these criteria.

Element	ΔR%	Crystal Structure	ΔElectro-negativity	Valence
Cu		**FCC**		**2+**
C	–44			

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H	–64			
O	–53			
Ag	+13	FCC	0	1+
Al	+12	FCC	-0.4	3+
Co	-2	HCP	-0.1	2+
Cr	-2	BCC	-0.3	3+
Fe	-3	BCC	-0.1	2+
Ni	-3	FCC	-0.1	2+
Pd	+8	FCC	+0.3	2+
Pt	+9	FCC	+0.3	2+
Zn	+4	HCP	-0.3	2+

(a) Ni, Pd, and Pt meet all of the criteria and thus form substitutional solid solutions having complete solubility. At elevated temperatures Co and Fe experience allotropic transformations to the FCC crystal structure, and thus display complete solid solubility at these temperatures.

(b) Ag, Al, Co, Cr, Fe, and Zn form substitutional solid solutions of incomplete solubility. All these metals have either BCC or HCP crystal structures, and/or the difference between their atomic radii and that for Cu are greater than ±15%, and/or have a valence different than 2+.

(c) C, H, and O form interstitial solid solutions. These elements have atomic radii that are significantly smaller than the atomic radius of Cu.

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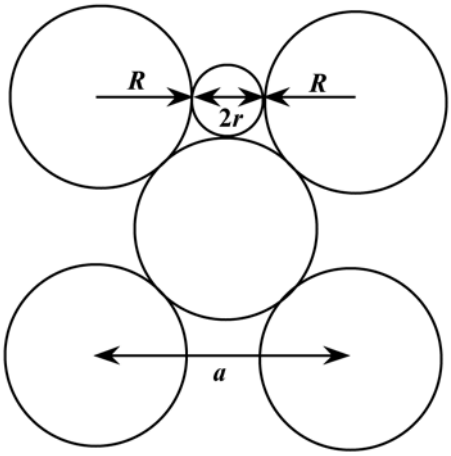
4.5 *For both FCC and BCC crystal structures, there are two different types of interstitial sites. In each case, one site is larger than the other, and is normally occupied by impurity atoms. For FCC, this larger one is located at the center of each edge of the unit cell; it is termed an octahedral interstitial site. On the other hand, with BCC the larger site type is found at* $0\ \frac{1}{2}\ \frac{1}{4}$ *positions—that is, lying on {100} faces, and situated midway between two unit cell edges on this face and one-quarter of the distance between the other two unit cell edges; it is termed a tetrahedral interstitial site. For both FCC and BCC crystal structures, compute the radius r of an impurity atom that will just fit into one of these sites in terms of the atomic radius R of the host atom.*

Solution

In the drawing below is shown the atoms on the (100) face of an FCC unit cell; the interstitial site is at the center of the edge.



The diameter of an atom that will just fit into this site ($2r$) is just the difference between that unit cell edge length (a) and the radii of the two host atoms that are located on either side of the site (R); that is

$$2r = a - 2R$$

However, for FCC a is related to R according to Equation 3.1 as $a = 2R\sqrt{2}$; therefore, solving for r from the above equation gives

$$r = \frac{a - 2R}{2} = \frac{2R\sqrt{2} - 2R}{2} = 0.41R$$

A (100) face of a BCC unit cell is shown below.

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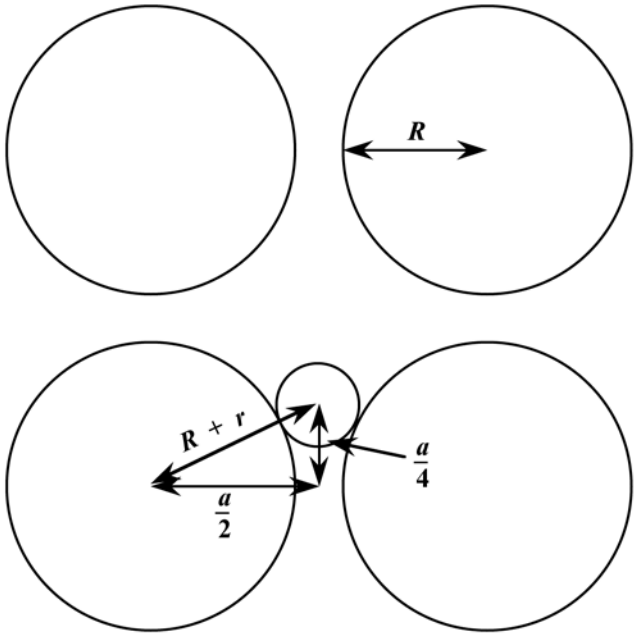

The interstitial atom that just fits into this interstitial site is shown by the small circle. It is situated in the plane of this (100) face, midway between the two vertical unit cell edges, and one quarter of the distance between the bottom and top cell edges. From the right triangle that is defined by the three arrows we may write

$$\left(\frac{a}{2}\right)^2 + \left(\frac{a}{4}\right)^2 = (R + r)^2$$

However, from Equation 3.3, $a = \frac{4R}{\sqrt{3}}$, and, therefore, making this substitution, the above equation takes the form

$$\left(\frac{4R}{2\sqrt{3}}\right)^2 + \left(\frac{4R}{4\sqrt{3}}\right)^2 = R^2 + 2Rr + r^2$$

After rearrangement the following quadratic equation results:

$$r^2 + 2Rr - 0.667R^2 = 0$$

And upon solving for *r:*

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$$r = \frac{-(2R) \pm \sqrt{(2R)^2 - (4)(1)(-0.667R^2)}}{2}$$

$$= \frac{-2R \pm 2.582R}{2}$$

And, finally

$$r(+) = \frac{-2R + 2.582R}{2} = 0.291R$$
$$r(-) = \frac{-2R - 2.582R}{2} = -2.291R$$

Of course, only the r(+) root is possible, and, therefore, $r = 0.291R$.

Thus, for a host atom of radius R, the size of an interstitial site for FCC is approximately 1.4 times that for BCC.

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Specification of Composition

4.6 *Derive the following equations:*

(a) Equation 4.7a

(b) Equation 4.9a

(c) Equation 4.10a

(d) Equation 4.11b

Solution

(a) This problem asks that we derive Equation 4.7a. To begin, C_1 is defined according to Equation 4.3 as

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100$$

or, equivalently

$$C_1 = \frac{m_1'}{m_1' + m_2'} \times 100$$

where the primed m's indicate masses in grams. From Equation 4.4 we may write

$$m_1' = n_{m1} A_1$$

$$m_2' = n_{m2} A_2$$

And, substitution into the C_1 expression above

$$C_1 = \frac{n_{m1} A_1}{n_{m1} A_1 + n_{m2} A_2} \times 100$$

From Equation 4.5 it is the case that

$$n_{m1} = \frac{C_1' (n_{m1} + n_{m2})}{100}$$

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$$n_{m2} = \frac{C_2'(n_{m1} + n_{m2})}{100}$$

And substitution of these expressions into the above equation leads to

$$C_1 = \frac{C_1' A_1}{C_1' A_1 + C_2' A_2} \times 100$$

which is just Equation 4.7a.

(b) This problem asks that we derive Equation 4.9a. To begin, C_1'' is defined as the mass of component 1 per unit volume of alloy, or

$$C_1'' = \frac{m_1}{V}$$

If we assume that the total alloy volume V is equal to the sum of the volumes of the two constituents--i.e., $V = V_1 + V_2$--then

$$C_1'' = \frac{m_1}{V_1 + V_2}$$

Furthermore, the volume of each constituent is related to its density and mass as

$$V_1 = \frac{m_1}{\rho_1}$$

$$V_2 = \frac{m_2}{\rho_2}$$

This leads to

$$C_1'' = \frac{m_1}{\frac{m_1}{\rho_1} + \frac{m_2}{\rho_2}}$$

From Equation 4.3, m_1 and m_2 may be expressed as follows:

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$$m_1 = \frac{C_1(m_1 + m_2)}{100}$$

$$m_2 = \frac{C_2(m_1 + m_2)}{100}$$

Substitution of these equations into the preceding expression yields

$$C_1'' = \frac{\dfrac{C_1(m_1 + m_2)}{100}}{\dfrac{\dfrac{C_1(m_1 + m_2)}{100}}{\rho_1} + \dfrac{\dfrac{C_2(m_1 + m_2)}{100}}{\rho_2}}$$

$$= \frac{C_1}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}}$$

If the densities ρ_1 and ρ_2 are given in units of g/cm^3, then conversion to units of kg/m^3 requires that we multiply this equation by 10^3, inasmuch as

$$1 \text{ g/cm}^3 = 10^3 \text{ kg/m}^3$$

Therefore, the previous equation takes the form

$$C_1'' = \frac{C_1}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}} \times 10^3$$

which is the desired expression.

(c) Now we are asked to derive Equation 4.10a. The density of an alloy ρ_{ave} is just the total alloy mass M divided by its volume V

$$\rho_{ave} = \frac{M}{V}$$

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Or, in terms of the component elements 1 and 2

$$\rho_{ave} = \frac{m_1 + m_2}{V_1 + V_2}$$

[*Note:* here it is assumed that the total alloy volume is equal to the separate volumes of the individual components, which is only an approximation; normally V will not be exactly equal to $(V_1 + V_2)$].

Each of V_1 and V_2 may be expressed in terms of its mass and density as,

$$V_1 = \frac{m_1}{\rho_1}$$

$$V_2 = \frac{m_2}{\rho_2}$$

When these expressions are substituted into the above equation, we get

$$\rho_{ave} = \frac{m_1 + m_2}{\frac{m_1}{\rho_1} + \frac{m_2}{\rho_2}}$$

Furthermore, from Equation 4.3

$$m_1 = \frac{C_1(m_1 + m_2)}{100}$$

$$m_2 = \frac{C_2(m_1 + m_2)}{100}$$

Which, when substituted into the above ρ_{ave} expression yields

$$\rho_{ave} = \frac{m_1 + m_2}{\frac{\frac{C_1(m_1 + m_2)}{100}}{\rho_1} + \frac{\frac{C_2(m_1 + m_2)}{100}}{\rho_2}}$$

And, finally, this equation reduces to

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$$= \frac{100}{\frac{C_1}{\rho_1} + \frac{C_2}{\rho_2}}$$

(d) And, finally, the derivation of Equation 4.11b for A_{ave} is requested. The alloy average molecular weight is just the ratio of total alloy mass in grams M' and the total number of moles in the alloy N_m. That is

$$A_{ave} = \frac{M\tilde{O}}{N_m} = \frac{m_1' + m_2'}{n_{m1} + n_{m2}}$$

But using Equation 4.4 we may write

$$m_1' = n_{m1} A_1$$

$$m_2' = n_{m2} A_2$$

Which, when substituted into the above A_{ave} expression yields

$$A_{ave} = \frac{M'}{N_m} = \frac{n_{m1} A_1 + n_{m2} A_2}{n_{m1} + n_{m2}}$$

Furthermore, from Equation 4.5

$$n_{m1} = \frac{C_1' (n_{m1} + n_{m2})}{100}$$

$$n_{m2} = \frac{C_2' (n_{m1} + n_{m2})}{100}$$

Thus, substitution of these expressions into the above equation for A_{ave} yields

$$A_{ave} = \frac{\frac{C_1' A_1 (n_{m1} + n_{m2})}{100} + \frac{C_2' A_2 (n_{m1} + n_{m2})}{100}}{n_{m1} + n_{m2}}$$

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$$= \frac{C_1' A_1 + C_2' A_2}{100}$$

which is the desired result.

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4.7 *What is the composition, in atom percent, of an alloy that consists of 30 wt% Zn and 70 wt% Cu?*

Solution

In order to compute composition, in atom percent, of a 30 wt% Zn-70 wt% Cu alloy, we employ Equation 4.6 as

$$C'_{Zn} = \frac{C_{Zn}A_{Cu}}{C_{Zn}A_{Cu} + C_{Cu}A_{Zn}} \times 100$$

$$= \frac{(30)(63.55\ \text{g/mol})}{(30)(63.55\ \text{g/mol}) + (70)(65.41\ \text{g/mol})} \times 100$$

$$= 29.4\ \text{at\%}$$

$$C'_{Cu} = \frac{C_{Cu}A_{Zn}}{C_{Zn}A_{Cu} + C_{Cu}A_{Zn}} \times 100$$

$$= \frac{(70)(65.41\ \text{g/mol})}{(30)(63.55\ \text{g/mol}) + (70)(65.41\ \text{g/mol})} \times 100$$

$$= 70.6\ \text{at\%}$$

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4.8 *What is the composition, in weight percent, of an alloy that consists of 6 at% Pb and 94 at% Sn?*

Solution

In order to compute composition, in weight percent, of a 6 at% Pb-94 at% Sn alloy, we employ Equation 4.7 as

$$C_{Pb} = \frac{C'_{Pb} A_{Pb}}{C'_{Pb} A_{Pb} + C'_{Sn} A_{Sn}} \times 100$$

$$= \frac{(6)(207.2\ g/mol)}{(6)(207.2\ g/mol) + (94)(118.71\ g/mol)} \times 100$$

$$= 10.0\ wt\%$$

$$C_{Sn} = \frac{C'_{Sn} A_{Sn}}{C'_{Pb} A_{Pb} + C'_{Sn} A_{Sn}} \times 100$$

$$= \frac{(94)(118.71\ g/mol)}{(6)(207.2\ g/mol) + (94)(118.71\ g/mol)} \times 100$$

$$= 90.0\ wt\%$$

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4.9 *Calculate the composition, in weight percent, of an alloy that contains 218.0 kg titanium, 14.6 kg of aluminum, and 9.7 kg of vanadium.*

Solution

The concentration, in weight percent, of an element in an alloy may be computed using a modified form of Equation 4.3. For this alloy, the concentration of titanium (C_{Ti}) is just

$$C_{Ti} = \frac{m_{Ti}}{m_{Ti} + m_{Al} + m_{V}} \times 100$$

$$= \frac{218 \text{ kg}}{218 \text{ kg} + 14.6 \text{ kg} + 9.7 \text{ kg}} \times 100 = 89.97 \text{ wt\%}$$

Similarly, for aluminum

$$C_{Al} = \frac{14.6 \text{ kg}}{218 \text{ kg} + 14.6 \text{ kg} + 9.7 \text{ kg}} \times 100 = 6.03 \text{ wt\%}$$

And for vanadium

$$C_{V} = \frac{9.7 \text{ kg}}{218 \text{ kg} + 14.6 \text{ kg} + 9.7 \text{ kg}} \times 100 = 4.00 \text{ wt\%}$$

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4.10 *What is the composition, in atom percent, of an alloy that contains 98 g tin and 65 g of lead?*

Solution

The concentration of an element in an alloy, in atom percent, may be computed using Equation 4.5. However, it first becomes necessary to compute the number of moles of both Sn and Pb, using Equation 4.4. Thus, the number of moles of Sn is just

$$n_{m_{\mathrm{Sn}}} = \frac{m'_{\mathrm{Sn}}}{A_{\mathrm{Sn}}} = \frac{98\ \mathrm{g}}{118.71\ \mathrm{g/mol}} = 0.826\ \mathrm{mol}$$

Likewise, for Pb

$$n_{m_{\mathrm{Pb}}} = \frac{65\ \mathrm{g}}{207.2\ \mathrm{g/mol}} = 0.314\ \mathrm{mol}$$

Now, use of Equation 4.5 yields

$$C'_{\mathrm{Sn}} = \frac{n_{m_{\mathrm{Sn}}}}{n_{m_{\mathrm{Sn}}} + n_{m_{\mathrm{Pb}}}} \times 100$$

$$= \frac{0.826\ \mathrm{mol}}{0.826\ \mathrm{mol} + 0.314\ \mathrm{mol}} \times 100 = 72.5\ \mathrm{at\%}$$

Also,

$$C'_{\mathrm{Pb}} = = \frac{0.314\ \mathrm{mol}}{0.826\ \mathrm{mol} + 0.314\ \mathrm{mol}} \times 100 = 27.5\ \mathrm{at\%}$$

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4.11 *What is the composition, in atom percent, of an alloy that contains 99.7 lb_m copper, 102 lb_m zinc, and 2.1 lb_m lead?*

Solution

In this problem we are asked to determine the concentrations, in atom percent, of the Cu-Zn-Pb alloy. It is first necessary to convert the amounts of Cu, Zn, and Pb into grams.

$$m'_{Cu} = (99.7\ lb_m)(453.6\ g/lb_m) = 45{,}224\ g$$

$$m'_{Zn} = (102\ lb_m)(453.6\ g/lb_m) = 46{,}267\ g$$

$$m'_{Pb} = (2.1\ lb_m)(453.6\ g/lb_m) = 953\ g$$

These masses must next be converted into moles (Equation 4.4), as

$$n_{m_{Cu}} = \frac{m'_{Cu}}{A_{Cu}} = \frac{45{,}224\ g}{63.55\ g/mol} = 711.6\ mol$$

$$n_{m_{Zn}} = \frac{46{,}267\ g}{65.41\ g/mol} = 707.3\ mol$$

$$n_{m_{Pb}} = \frac{953\ g}{207.2\ g/mol} = 4.6\ mol$$

Now, employment of a modified form of Equation 4.5, gives

$$C'_{Cu} = \frac{n_{m_{Cu}}}{n_{m_{Cu}} + n_{m_{Zn}} + n_{m_{Pb}}} \times 100$$

$$= \frac{711.6\ mol}{711.6\ mol + 707.3\ mol + 4.6\ mol} \times 100 = 50.0\ at\%$$

$$C'_{Zn} = \frac{707.3\ mol}{711.6\ mol + 707.3\ mol + 4.6\ mol} \times 100 = 49.7\ at\%$$

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$$C'_{Pb} = \frac{4.6 \text{ mol}}{711.6 \text{ mol} + 707.3 \text{ mol} + 4.6 \text{ mol}} \times 100 = 0.3 \text{ at\%}$$

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4.12 *What is the composition, in atom percent, of an alloy that consists of 97 wt% Fe and 3 wt% Si?*

Solution

We are asked to compute the composition of an Fe-Si alloy in atom percent. Employment of Equation 4.6 leads to

$$C'_{Fe} = \frac{C_{Fe}A_{Si}}{C_{Fe}A_{Si} + C_{Si}A_{Fe}} \times 100$$

$$= \frac{97(28.09\ g/mol)}{97(28.09\ g/mol) + 3(55.85\ g/mol)} \times 100$$

$$= 94.2\ at\%$$

$$C'_{Si} = \frac{C_{Si}A_{Fe}}{C_{Si}A_{Fe} + C_{Fe}A_{Si}} \times 100$$

$$= \frac{3(55.85\ g/mol)}{3(55.85\ g/mol) + 97(28.09\ g/mol)} \times 100$$

$$= 5.8\ at\%$$

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4.13 *Convert the atom percent composition in Problem 4.11 to weight percent.*

Solution

The composition in atom percent for Problem 4.11 is 50.0 at% Cu, 49.7 at% Zn, and 0.3 at% Pb. Modification of Equation 4.7 to take into account a three-component alloy leads to the following

$$C_{Cu} = \frac{C'_{Cu} A_{Cu}}{C'_{Cu} A_{Cu} + C'_{Zn} A_{Zn} + C'_{Pb} A_{Pb}} \times 100$$

$$= \frac{(50.0)(63.55\ \text{g/mol})}{(50.0)(63.55\ \text{g/mol}) + (49.7)(65.41\ \text{g/mol}) + (0.3)(207.2\ \text{g/mol})} \times 100$$

$$= 49.0\ \text{wt\%}$$

$$C_{Zn} = \frac{C'_{Zn} A_{Zn}}{C'_{Cu} A_{Cu} + C'_{Zn} A_{Zn} + C'_{Pb} A_{Pb}} \times 100$$

$$= \frac{(49.7)(65.41\ \text{g/mol})}{(50.0)(63.55\ \text{g/mol}) + (49.7)(65.41\ \text{g/mol}) + (0.3)(207.2\ \text{g/mol})} \times 100$$

$$= 50.1\ \text{wt\%}$$

$$C_{Pb} = \frac{C'_{Pb} A_{Pb}}{C'_{Cu} A_{Cu} + C'_{Zn} A_{Zn} + C'_{Pb} A_{Pb}} \times 100$$

$$= \frac{(0.3)(207.2\ \text{g/mol})}{(50.0)(63.55\ \text{g/mol}) + (49.7)(65.41\ \text{g/mol}) + (0.3)(207.2\ \text{g/mol})} \times 100$$

$$= 1.0\ \text{wt\%}$$

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4.14 *Calculate the number of atoms per cubic meter in aluminum.*

Solution

In order to solve this problem, one must employ Equation 4.2,

$$N = \frac{N_A \rho_{Al}}{A_{Al}}$$

The density of Al (from the table inside of the front cover) is 2.71 g/cm^3, while its atomic weight is 26.98 g/mol. Thus,

$$N = \frac{(6.022 \times 10^{23} \text{ atoms/mol})(2.71 \text{ g/cm}^3)}{26.98 \text{ g/mol}}$$

$$= 6.05 \times 10^{22} \text{ atoms/cm}^3 = 6.05 \times 10^{28} \text{ atoms/m}^3$$

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4.15 *The concentration of carbon in an iron-carbon alloy is 0.15 wt%. What is the concentration in kilograms of carbon per cubic meter of alloy?*

Solution

In order to compute the concentration in kg/m^3 of C in a 0.15 wt% C-99.85 wt% Fe alloy we must employ Equation 4.9 as

$$C''_C = \frac{C_C}{\frac{C_C}{\rho_C} + \frac{C_{Fe}}{\rho_{Fe}}} \times 10^3$$

From inside the front cover, densities for carbon and iron are 2.25 and 7.87 g/cm^3, respectively; and, therefore

$$C''_C = \frac{0.15}{\frac{0.15}{2.25\ g/cm^3} + \frac{99.85}{7.87\ g/cm^3}} \times 10^3$$

$$= 11.8\ kg/m^3$$

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4.16 *Determine the approximate density of a high-leaded brass that has a composition of 64.5 wt% Cu, 33.5 wt% Zn, and 2.0 wt% Pb.*

Solution

In order to solve this problem, Equation 4.10a is modified to take the following form:

$$\rho_{ave} = \frac{100}{\frac{C_{Cu}}{\rho_{Cu}} + \frac{C_{Zn}}{\rho_{Zn}} + \frac{C_{Pb}}{\rho_{Pb}}}$$

And, using the density values for Cu, Zn, and Pb—i.e., 8.94 g/cm^3, 7.13 g/cm^3, and 11.35 g/cm^3—(as taken from inside the front cover of the text), the density is computed as follows:

$$\rho_{ave} = \frac{100}{\frac{64.5\ \text{wt\%}}{8.94\ \text{g/cm}^3} + \frac{33.5\ \text{wt\%}}{7.13\ \text{g/cm}^3} + \frac{2.0\ \text{wt\%}}{11.35\ \text{g/cm}^3}}$$

$$= 8.27\ \text{g/cm}^3$$

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4.17 *Calculate the unit cell edge length for an 85 wt% Fe-15 wt% V alloy. All of the vanadium is in solid solution, and, at room temperature the crystal structure for this alloy is BCC.*

Solution

In order to solve this problem it is necessary to employ Equation 3.5; in this expression density and atomic weight will be averages for the alloy—that is

$$\rho_{ave} = \frac{nA_{ave}}{V_C N_A}$$

Inasmuch as the unit cell is cubic, then $V_C = a^3$, then

$$\rho_{ave} = \frac{nA_{ave}}{a^3 N_A}$$

And solving this equation for the unit cell edge length, leads to

$$a = \left(\frac{nA_{ave}}{\rho_{ave} N_A} \right)^{1/3}$$

Expressions for A_{ave} and ρ_{ave} are found in Equations 4.11a and 4.10a, respectively, which, when incorporated into the above expression yields

$$a = \left[\frac{n \left(\dfrac{100}{\dfrac{C_{Fe}}{A_{Fe}} + \dfrac{C_V}{A_V}} \right)}{\left(\dfrac{100}{\dfrac{C_{Fe}}{\rho_{Fe}} + \dfrac{C_V}{\rho_V}} \right) N_A} \right]^{1/3}$$

Since the crystal structure is BCC, the value of n in the above expression is 2 atoms per unit cell. The atomic weights for Fe and V are 55.85 and 50.94 g/mol, respectively (Figure 2.6), whereas the densities for the Fe and V are 7.87 g/cm^3 and 6.10 g/cm^3 (from inside the front cover). Substitution of these, as well as the concentration values stipulated in the problem statement, into the above equation gives

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$$a = \left[\frac{(2 \text{ atoms/unit cell}) \left(\dfrac{100}{\dfrac{85 \text{ wt\%}}{55.85 \text{ g/mol}} + \dfrac{15 \text{ wt\%}}{50.94 \text{ g/mol}}} \right)}{\left(\dfrac{100}{\dfrac{85 \text{ wt\%}}{7.87 \text{ g/cm}^3} + \dfrac{15 \text{ wt\%}}{6.10 \text{ g/cm}^3}} \right) \left(6.022 \times 10^{23} \text{ atoms/mol}\right)} \right]^{1/3}$$

$$= 2.89 \times 10^{-8} \text{ cm} = 0.289 \text{ nm}$$

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4.18 *Some hypothetical alloy is composed of 12.5 wt% of metal A and 87.5 wt% of metal B. If the densities of metals A and B are 4.27 and 6.35 g/cm^3, respectively, whereas their respective atomic weights are 61.4 and 125.7 g/mol, determine whether the crystal structure for this alloy is simple cubic, face-centered cubic, or body-centered cubic. Assume a unit cell edge length of 0.395 nm.*

Solution

In order to solve this problem it is necessary to employ Equation 3.5; in this expression density and atomic weight will be averages for the alloy—that is

$$\rho_{ave} = \frac{nA_{ave}}{V_C N_A}$$

Inasmuch as for each of the possible crystal structures, the unit cell is cubic, then $V_C = a^3$, or

$$\rho_{ave} = \frac{nA_{ave}}{a^3 N_A}$$

And, in order to determine the crystal structure it is necessary to solve for n, the number of atoms per unit cell. For n =1, the crystal structure is simple cubic, whereas for n values of 2 and 4, the crystal structure will be either BCC or FCC, respectively. When we solve the above expression for n the result is as follows:

$$n = \frac{\rho_{ave} a^3 N_A}{A_{ave}}$$

Expressions for A_{ave} and ρ_{ave} are found in Equations 4.11a and 4.10a, respectively, which, when incorporated into the above expression yields

$$n = \frac{\left(\dfrac{100}{\dfrac{C_A}{\rho_A} + \dfrac{C_B}{\rho_B}}\right) a^3 N_A}{\left(\dfrac{100}{\dfrac{C_A}{A_A} + \dfrac{C_B}{A_B}}\right)}$$

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Substitution of the concentration values (i.e., C_A = 12.5 wt% and C_B = 87.5 wt%) as well as values for the other parameters given in the problem statement, into the above equation gives

$$n = \frac{\left(\frac{100}{\frac{12.5\ \text{wt\%}}{4.27\ \text{g/cm}^3} + \frac{87.5\ \text{wt\%}}{6.35\ \text{g/cm}^3}}\right)(3.95 \times 10^{-8}\ \text{nm})^3(6.022 \times 10^{23}\ \text{atoms/mol})}{\left(\frac{100}{\frac{12.5\ \text{wt\%}}{61.4\ \text{g/mol}} + \frac{87.5\ \text{wt\%}}{125.7\ \text{g/mol}}}\right)}$$

$$= 2.00\ \text{atoms/unit cell}$$

Therefore, on the basis of this value, the crystal structure is *body-centered cubic*.

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4.19 *For a solid solution consisting of two elements (designated as 1 and 2), sometimes it is desirable to determine the number of atoms per cubic centimeter of one element in a solid solution, N_1, given the concentration of that element specified in weight percent, C_1. This computation is possible using the following expression:*

$$N_1 = \frac{N_A C_1}{\frac{C_1 A_1}{\rho_1} + \frac{A_1}{\rho_2}(100 - C_1)} \qquad (4.18)$$

where

N_A = *Avogadro's number*

ρ_1 *and* ρ_2 = *densities of the two elements*

A_1 = *the atomic weight of element 1*

Derive Equation 4.18 using Equation 4.2 and expressions contained in Section 4.4.

Solution

This problem asks that we derive Equation 4.18, using other equations given in the chapter. The concentration of component 1 in atom percent (C_1') is just $100\,c_1'$ where c_1' is the atom fraction of component 1. Furthermore, c_1' is defined as $c_1' = N_1/N$ where N_1 and N are, respectively, the number of atoms of component 1 and total number of atoms per cubic centimeter. Thus, from the above discussion the following holds:

$$N_1 = \frac{C_1' N}{100}$$

Substitution into this expression of the appropriate form of N from Equation 4.2 yields

$$N_1 = \frac{C_1' N_A \rho_{ave}}{100 A_{ave}}$$

And, finally, substitution into this equation expressions for C_1' (Equation 4.6a), ρ_{ave} (Equation 4.10a), A_{ave} (Equation 4.11a), and realizing that $C_2 = (C_1 - 100)$, and after some algebraic manipulation we obtain the desired expression:

$$N_1 = \frac{N_A C_1}{\frac{C_1 A_1}{\rho_1} + \frac{A_1}{\rho_2}(100 - C_1)}$$

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4.20 *Gold forms a substitutional solid solution with silver. Compute the number of gold atoms per cubic centimeter for a silver-gold alloy that contains 10 wt% Au and 90 wt% Ag. The densities of pure gold and silver are 19.32 and 10.49 g/cm^3, respectively.*

Solution

To solve this problem, employment of Equation 4.18 is necessary, using the following values:

$C_1 = C_{Au} = 10$ wt%
$\rho_1 = \rho_{Au} = 19.32$ g/cm^3
$\rho_2 = \rho_{Ag} = 10.49$ g/cm^3
$A_1 = A_{Au} = 196.97$ g/mol

Thus

$$N_{Au} = \frac{N_A C_{Au}}{\frac{C_{Au} A_{Au}}{\rho_{Au}} + \frac{A_{Au}}{\rho_{Ag}}(100 - C_{Au})}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})\ (10 \text{ wt\%})}{\frac{(10 \text{ wt\%})(196.97 \text{ g/mol})}{19.32 \text{ g/cm}^3} + \frac{196.97 \text{ g/mol}}{10.49 \text{ g/cm}^3}(100 - 10 \text{ wt\%})}$$

$$= 3.36 \times 10^{21} \text{ atoms/cm}^3$$

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4.21 *Germanium forms a substitutional solid solution with silicon. Compute the number of germanium atoms per cubic centimeter for a germanium-silicon alloy that contains 15 wt% Ge and 85 wt% Si. The densities of pure germanium and silicon are 5.32 and 2.33 g/cm^3, respectively.*

Solution

To solve this problem, employment of Equation 4.18 is necessary, using the following values:

$C_1 = C_{Ge} = 15$ wt%
$\rho_1 = \rho_{Ge} = 5.32$ g/cm^3
$\rho_2 = \rho_{Si} = 2.33$ g/cm^3
$A_1 = A_{Ge} = 72.64$ g/mol

Thus

$$N_{Ge} = \frac{N_A C_{Ge}}{\frac{C_{Ge} A_{Ge}}{\rho_{Ge}} + \frac{A_{Ge}}{\rho_{Si}}(100 - C_{Ge})}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(15 \text{ wt\%})}{\frac{(15 \text{ wt\%})(72.64 \text{ g/mol})}{5.32 \text{ g/cm}^3} + \frac{72.64 \text{ g/mol}}{2.33 \text{ g/cm}^3}(100 - 15 \text{ wt\%})}$$

$$= 3.16 \times 10^{21} \text{ atoms/cm}^3$$

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4.22 *Sometimes it is desirable to be able to determine the weight percent of one element, C_1, that will produce a specified concentration in terms of the number of atoms per cubic centimeter, N_1, for an alloy composed of two types of atoms. This computation is possible using the following expression:*

$$C_1 = \frac{100}{1 + \frac{N_A \rho_2}{N_1 A_1} - \frac{\rho_2}{\rho_1}} \tag{4.19}$$

where

N_A = *Avogadro's number*

ρ_1 *and* ρ_2 = *densities of the two elements*

A_1 *and* A_2 = *the atomic weights of the two elements*

Derive Equation 4.19 using Equation 4.2 and expressions contained in Section 4.4.

Solution

The number of atoms of component 1 per cubic centimeter is just equal to the atom fraction of component 1 (c_1') times the total number of atoms per cubic centimeter in the alloy (N). Thus, using the equivalent of Equation 4.2, we may write

$$N_1 = c_1' N = \frac{c_1' N_A \rho_{ave}}{A_{ave}}$$

Realizing that

$$c_1' = \frac{C_1'}{100}$$

and

$$C_2' = 100 - C_1'$$

and substitution of the expressions for ρ_{ave} and A_{ave}, Equations 4.10b and 4.11b, respectively, leads to

$$N_1 = \frac{c_1' N_A \rho_{ave}}{A_{ave}}$$

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$$= \frac{N_A C_1' \rho_1 \rho_2}{C_1' \rho_2 A_1 + (100 - C_1') \rho_1 A_2}$$

And, solving for C_1'

$$C_1' = \frac{100\ N_1 \rho_1 A_2}{N_A \rho_1 \rho_2 - N_1 \rho_2 A_1 + N_1 \rho_1 A_2}$$

Substitution of this expression for C_1' into Equation 4.7a, which may be written in the following form

$$C_1 = \frac{C_1' A_1}{C_1' A_1 + C_2' A_2} \times 100$$

$$= \frac{C_1' A_1}{C_1' A_1 + (100 - C_1') A_2} \times 100$$

yields

$$C_1 = \frac{100}{1 + \frac{N_A \rho_2}{N_1 A_1} - \frac{\rho_2}{\rho_1}}$$

the desired expression.

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4.23 *Molybdenum forms a substitutional solid solution with tungsten. Compute the weight percent of molybdenum that must be added to tungsten to yield an alloy that contains* 1.0×10^{22} *Mo atoms per cubic centimeter. The densities of pure Mo and W are 10.22 and 19.30 g/cm*^{3}*, respectively.*

Solution

To solve this problem, employment of Equation 4.19 is necessary, using the following values:

$N_1 = N_{Mo} = 10^{22}$ atoms/cm^3
$\rho_1 = \rho_{Mo} = 10.22$ g/cm^3
$\rho_2 = \rho_W = 19.30$ g/cm^3
$A_1 = A_{Mo} = 95.94$ g/mol
$A_2 = A_W = 183.84$ g/mol

Thus

$$C_{Mo} = \frac{100}{1 + \frac{N_A \rho_W}{N_{Mo} A_{Mo}} - \frac{\rho_W}{\rho_{Mo}}}$$

$$= \frac{100}{1 + \frac{(6.022 \times 10^{23} \text{ atoms/mol})(19.30 \text{ g/cm}^3)}{(10^{22} \text{ atoms/cm}^3)(95.94 \text{ g/mol})} - \left(\frac{19.30 \text{ g/cm}^3}{10.22 \text{ g/cm}^3}\right)}$$

$$= 8.91 \text{ wt\%}$$

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4.24 *Niobium forms a substitutional solid solution with vanadium. Compute the weight percent of niobium that must be added to vanadium to yield an alloy that contains 1.55×10^{22} Nb atoms per cubic centimeter. The densities of pure Nb and V are 8.57 and 6.10 g/cm^3, respectively.*

Solution

To solve this problem, employment of Equation 4.19 is necessary, using the following values:

$N_1 = N_{Nb} = 1.55 \times 10^{22}$ atoms/cm^3
$\rho_1 = \rho_{Nb} = 8.57$ g/cm^3
$\rho_2 = \rho_V = 6.10$ g/cm^3
$A_1 = A_{Nb} = 92.91$ g/mol
$A_2 = A_V = 50.94$ g/mol

Thus

$$C_{Nb} = \frac{100}{1 + \frac{N_A \rho_V}{N_{Nb} A_{Nb}} - \frac{\rho_V}{\rho_{Nb}}}$$

$$= \frac{100}{1 + \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(6.10\ \text{g/cm}^3)}{(1.55 \times 10^{22}\ \text{atoms/cm}^3)(92.91\ \text{g/mol})} - \left(\frac{6.10\ \text{g/cm}^3}{8.57\ \text{g/cm}^3}\right)}$$

$$= 35.2\ \text{wt\%}$$

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4.25 *Silver and palladium both have the FCC crystal structure, and Pd forms a substitutional solid solution for all concentrations at room temperature. Compute the unit cell edge length for a 75 wt% Ag–25 wt% Pd alloy. The room-temperature density of Pd is 12.02 g/cm^3, and its atomic weight and atomic radius are 106.4 g/mol and 0.138 nm, respectively.*

Solution

First of all, the atomic radii for Ag (using the table inside the front cover) and Pd are 0.144 and 0.138 nm, respectively. Also, using Equation 3.5 it is possible to compute the unit cell volume, and inasmuch as the unit cell is cubic, the unit cell edge length is just the cube root of the volume. However, it is first necessary to calculate the density and average atomic weight of this alloy using Equations 4.10a and 4.11a. Inasmuch as the densities of silver and palladium are 10.49 g/cm^3 (as taken from inside the front cover) and 12.02 g/cm^3, respectively, the average density is just

$$\rho_{ave} = \frac{100}{\frac{C_{Ag}}{\rho_{Ag}} + \frac{C_{Pd}}{\rho_{Pd}}}$$

$$= \frac{100}{\frac{75 \text{ wt\%}}{10.49 \text{ g/cm}^3} + \frac{25 \text{ wt\%}}{12.02 \text{ g/cm}^3}}$$

$$= 10.83 \text{ g/cm}^3$$

And for the average atomic weight

$$A_{ave} = \frac{100}{\frac{C_{Ag}}{A_{Ag}} + \frac{C_{Pd}}{A_{Pd}}}$$

$$= \frac{100}{\frac{75 \text{ wt\%}}{107.9 \text{ g/mol}} + \frac{25 \text{ wt\%}}{106.4 \text{ g/mol}}}$$

$$= 107.5 \text{ g/mol}$$

Now, V_C is determined from Equation 3.5 as

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$$V_C = \frac{nA_{ave}}{\rho_{ave} N_A}$$

$$= \frac{(4 \text{ atoms/unit cell})(107.5 \text{ g/mol})}{(10.83 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 6.59 \times 10^{-23} \text{ cm}^3\text{/unit cell}$$

And, finally

$$a = (V_C)^{1/3}$$

$$= (6.59 \times 10^{-23} \text{cm}^3\text{/unit cell})^{1/3}$$

$$= 4.04 \times 10^{-8} \text{ cm} = 0.404 \text{ nm}$$

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Dislocations—Linear Defects

4.26 *Cite the relative Burgers vector–dislocation line orientations for edge, screw, and mixed dislocations.*

Solution

The Burgers vector and dislocation line are perpendicular for edge dislocations, parallel for screw dislocations, and neither perpendicular nor parallel for mixed dislocations.

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Interfacial Defects

4.27 *For an FCC single crystal, would you expect the surface energy for a* (*100*) *plane to be greater or less than that for a* (*111*) *plane? Why? (Note: You may want to consult the solution to Problem 3.54 at the end of Chapter 3.)*

Solution

The surface energy for a crystallographic plane will depend on its packing density [i.e., the planar density (Section 3.11)]—that is, the higher the packing density, the greater the number of nearest-neighbor atoms, and the more atomic bonds in that plane that are satisfied, and, consequently, the lower the surface energy. From the solution to Problem 3.54, planar densities for FCC (100) and (111) planes are $\frac{1}{4R^2}$ and $\frac{1}{2R^2\sqrt{3}}$, respectively—that is $\frac{0.25}{R^2}$ and $\frac{0.29}{R^2}$ (where R is the atomic radius). Thus, since the planar density for (111) is greater, it will have the lower surface energy.

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4.28 *For a BCC single crystal, would you expect the surface energy for a* (*100*) *plane to be greater or less than that for a* (*110*) *plane? Why? (Note: You may want to consult the solution to Problem 3.55 at the end of Chapter 3.)*

Solution

The surface energy for a crystallographic plane will depend on its packing density [i.e., the planar density (Section 3.11)]—that is, the higher the packing density, the greater the number of nearest-neighbor atoms, and the more atomic bonds in that plane that are satisfied, and, consequently, the lower the surface energy. From the solution to Problem 3.55, the planar densities for BCC (100) and (110) are $\frac{3}{16R^2}$ and $\frac{3}{8R^2\sqrt{2}}$, respectively—that is $\frac{0.19}{R^2}$ and $\frac{0.27}{R^2}$. Thus, since the planar density for (110) is greater, it will have the lower surface energy.

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4.29 *(a) For a given material, would you expect the surface energy to be greater than, the same as, or less than the grain boundary energy? Why?*

(b) The grain boundary energy of a small-angle grain boundary is less than for a high-angle one. Why is this so?

Solution

(a) The surface energy will be greater than the grain boundary energy. For grain boundaries, some atoms on one side of a boundary will bond to atoms on the other side; such is not the case for surface atoms. Therefore, there will be fewer unsatisfied bonds along a grain boundary.

(b) The small-angle grain boundary energy is lower than for a high-angle one because more atoms bond across the boundary for the small-angle, and, thus, there are fewer unsatisfied bonds.

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4.30 *(a) Briefly describe a twin and a twin boundary.*

(b) Cite the difference between mechanical and annealing twins.

Solution

(a) A twin boundary is an interface such that atoms on one side are located at mirror image positions of those atoms situated on the other boundary side. The region on one side of this boundary is called a twin.

(b) Mechanical twins are produced as a result of mechanical deformation and generally occur in BCC and HCP metals. Annealing twins form during annealing heat treatments, most often in FCC metals.

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4.31 *For each of the following stacking sequences found in FCC metals, cite the type of planar defect that exists:*

(a) . . . A B C A B C B A C B A . . .

(b) . . . A B C A B C B C A B C . . .

Now, copy the stacking sequences and indicate the position(s) of planar defect(s) with a vertical dashed line.

Solution

(a) The interfacial defect that exists for this stacking sequence is a twin boundary, which occurs at the indicated position.

The stacking sequence on one side of this position is mirrored on the other side.

(b) The interfacial defect that exists within this FCC stacking sequence is a stacking fault, which occurs between the two lines.

Within this region, the stacking sequence is HCP.

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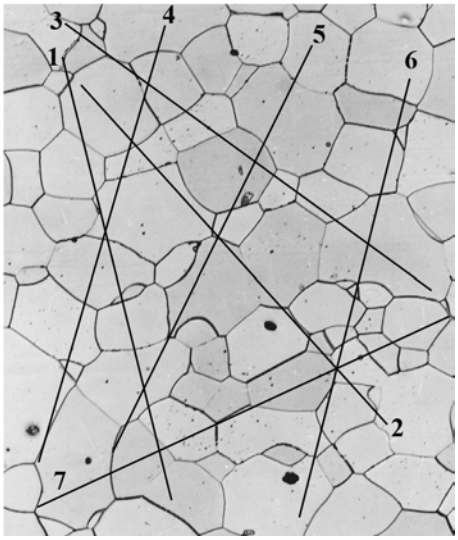
Grain Size Determination

4.32 *(a) Using the intercept method, determine the average grain size, in millimeters, of the specimen whose microstructure is shown in Figure 4.14(b); use at least seven straight-line segments.*

(b) Estimate the ASTM grain size number for this material.

Solution

(a) Below is shown the photomicrograph of Figure 4.14(*b*), on which seven straight line segments, each of which is 60 mm long has been constructed; these lines are labeled "1" through "7".



In order to determine the average grain diameter, it is necessary to count the number of grains intersected by each of these line segments. These data are tabulated below.

Line Number	No. Grains Intersected
1	11
2	10
3	9
4	8.5
5	7
6	10
7	8

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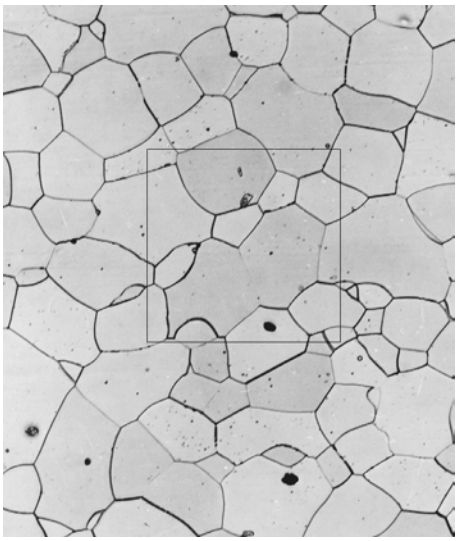
The average number of grain boundary intersections for these lines was 9.1. Therefore, the average line length intersected is just

$$\frac{60 \text{ mm}}{9.1} = 6.59 \text{ mm}$$

Hence, the average grain diameter, d, is

$$d = \frac{\text{ave. line length intersected}}{\text{magnification}} = \frac{6.59 \text{ mm}}{100} = 6.59 \times 10^{-2} \text{ mm}$$

(b) This portion of the problem calls for us to estimate the ASTM grain size number for this same material. The average grain size number, n, is related to the number of grains per square inch, N, at a magnification of 100× according to Equation 4.16. Inasmuch as the magnification is 100×, the value of N is measured directly from the micrograph. The photomicrograph on which has been constructed a square 1 in. on a side is shown below.



The total number of complete grains within this square is approximately 10 (taking into account grain fractions). Now, in order to solve for n in Equation 4.16, it is first necessary to take logarithms as

$$\log N = (n - 1) \log 2$$

From which n equals

$$n = \frac{\log N}{\log 2} + 1$$

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$$= \frac{\log 10}{\log 2} + 1 = 4.3$$

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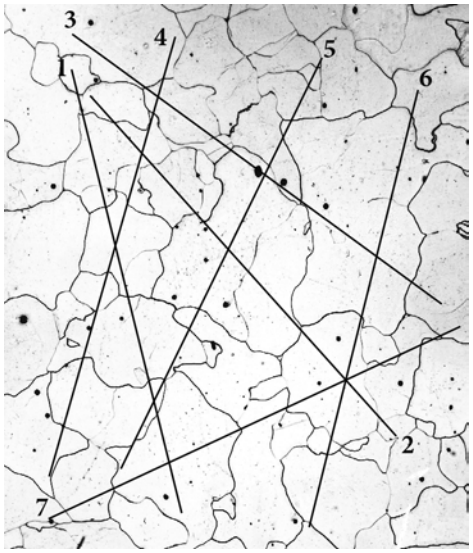
4.33 *(a) Employing the intercept technique, determine the average grain size for the steel specimen whose microstructure is shown in Figure 9.25(a); use at least seven straight-line segments.*

(b) Estimate the ASTM grain size number for this material.

Solution

(a) Below is shown the photomicrograph of Figure 9.25(*a*), on which seven straight line segments, each of which is 60 mm long has been constructed; these lines are labeled "1" through "7".



In order to determine the average grain diameter, it is necessary to count the number of grains intersected by each of these line segments. These data are tabulated below.

Line Number	No. Grains Intersected
1	7
2	7
3	7
4	8
5	10
6	7
7	8

The average number of grain boundary intersections for these lines was 8.7. Therefore, the average line length intersected is just

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$$\frac{60 \text{ mm}}{8.7} = 6.9 \text{ mm}$$

Hence, the average grain diameter, d, is

$$d = \frac{\text{ave. line length intersected}}{\text{magnification}} = \frac{6.9 \text{ mm}}{90} = 0.077 \text{ mm}$$

(b) This portion of the problem calls for us to estimate the ASTM grain size number for this same material. The average grain size number, n, is related to the number of grains per square inch, N, at a magnification of 100× according to Equation 4.16. However, the magnification of this micrograph is not 100×, but rather 90×. Consequently, it is necessary to use Equation 4.17

$$N_M \left(\frac{M}{100} \right)^2 = 2^{n-1}$$

where N_M = the number of grains per square inch at magnification M, and n is the ASTM grain size number. Taking logarithms of both sides of this equation leads to the following:

$$\log N_M + 2 \log \left(\frac{M}{100} \right) = (n - 1) \log 2$$

Solving this expression for n gives

$$n = \frac{\log N_M + 2 \log \left(\frac{M}{100} \right)}{\log 2} + 1$$

The photomicrograph on which has been constructed a square 1 in. on a side is shown below.

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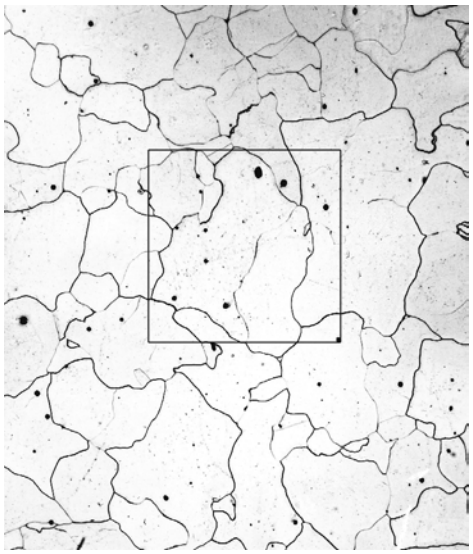

From Figure 9.25(a), N_M is measured to be approximately 7, which leads to

$$n = \frac{\log 7 + 2 \log\left(\frac{90}{100}\right)}{\log 2} + 1$$

$$= 3.5$$

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4.34 *For an ASTM grain size of 8, approximately how many grains would there be per square inch at*

(a) a magnification of 100, and

(b) without any magnification?

Solution

(a) This part of problem asks that we compute the number of grains per square inch for an ASTM grain size of 8 at a magnification of 100×. All we need do is solve for the parameter N in Equation 4.16, inasmuch as n = 8. Thus

$$N = 2^{n-1}$$

$$= 2^{8-1} = 128 \text{ grains/in.}^2$$

(b) Now it is necessary to compute the value of N for no magnification. In order to solve this problem it is necessary to use Equation 4.17:

$$N_M\left(\frac{M}{100}\right)^2 = 2^{n-1}$$

where N_M = the number of grains per square inch at magnification M, and n is the ASTM grain size number. Without any magnification, M in the above equation is 1, and therefore,

$$N_1\left(\frac{1}{100}\right)^2 = 2^{8-1} = 128$$

And, solving for N_1, N_1 = 1,280,000 grains/in.^{2}.

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4.35 *Determine the ASTM grain size number if 25 grains per square inch are measured at a magnification of 600.*

Solution

This problem asks that we determine the ASTM grain size number if 8 grains per square inch are measured at a magnification of 600. In order to solve this problem we make use of Equation 4.17:

$$N_M \left(\frac{M}{100} \right)^2 = 2^{n-1}$$

where N_M = the number of grains per square inch at magnification M, and n is the ASTM grain size number. Solving the above equation for n, and realizing that $N_M = 8$, while $M = 600$, we have

$$n = \frac{\log N_M + 2 \log \left(\frac{M}{100} \right)}{\log 2} + 1$$

$$= \frac{\log 8 + 2 \log \left(\frac{600}{100} \right)}{\log 2} + 1 = 9.2$$

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4.36 *Determine the ASTM grain size number if 20 grains per square inch are measured at a magnification of 50.*

Solution

This problem asks that we determine the ASTM grain size number if 20 grains per square inch are measured at a magnification of 50. In order to solve this problem we make use of Equation 4.17—viz.

$$N_M\left(\frac{M}{100}\right)^2 = 2^{n-1}$$

where N_M = the number of grains per square inch at magnification M, and n is the ASTM grain size number. Solving the above equation for n, and realizing that $N_M = 20$, while $M = 50$, we have

$$n = \frac{\log N_M + 2 \log\left(\frac{M}{100}\right)}{\log 2} + 1$$

$$= \frac{\log 20 + 2 \log\left(\frac{50}{100}\right)}{\log 2} + 1 = 3.3$$

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DESIGN PROBLEMS

Specification of Composition

4.D1 *Aluminum–lithium alloys have been developed by the aircraft industry to reduce the weight and improve the performance of its aircraft. A commercial aircraft skin material having a density of 2.55 g/cm^3 is desired. Compute the concentration of Li (in wt%) that is required.*

Solution

Solution of this problem requires the use of Equation 4.10a, which takes the form

$$\rho_{ave} = \frac{100}{\frac{C_{Li}}{\rho_{Li}} + \frac{100 - C_{Li}}{\rho_{Al}}}$$

inasmuch as $C_{Li} + C_{Al} = 100$. According to the table inside the front cover, the respective densities of Li and Al are 0.534 and 2.71 g/cm^3. Upon solving for C_{Li} from the above equation, we get

$$C_{Li} = \frac{100\ \rho_{Li}(\rho_{Al} - \rho_{ave})}{\rho_{ave}(\rho_{Al} - \rho_{Li})}$$

And incorporating specified values into the above equation leads to

$$C_{Li} = \frac{(100)(0.534\ \text{g/cm}^3)(2.71\ \text{g/cm}^3 - 2.55\ \text{g/cm}^3)}{(2.55\ \text{g/cm}^3)(2.71\ \text{g/cm}^3 - 0.534\ \text{g/cm}^3)}$$

$$= 1.540\ \text{wt\%}$$

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4.D2 *Iron and vanadium both have the BCC crystal structure and V forms a substitutional solid solution in Fe for concentrations up to approximately 20 wt% V at room temperature. Determine the concentration in weight percent of V that must be added to iron to yield a unit cell edge length of 0.289 nm.*

Solution

To begin, it is necessary to employ Equation 3.5, and solve for the unit cell volume, V_C, as

$$V_C = \frac{nA_{ave}}{\rho_{ave} N_A}$$

where A_{ave} and ρ_{ave} are the atomic weight and density, respectively, of the Fe-V alloy. Inasmuch as both of these materials have the BCC crystal structure, which has cubic symmetry, V_C is just the cube of the unit cell length, a. That is

$$V_C = a^3 = (0.289 \text{ nm})^3$$

$$= (2.89 \times 10^{-8} \text{ cm})^3 = 2.414 \times 10^{-23} \text{ cm}^3$$

It is now necessary to construct expressions for A_{ave} and ρ_{ave} in terms of the concentration of vanadium, C_V, using Equations 4.11a and 4.10a. For A_{ave} we have

$$A_{ave} = \frac{100}{\frac{C_V}{A_V} + \frac{(100 - C_V)}{A_{Fe}}}$$

$$= \frac{100}{\frac{C_V}{50.94 \text{ g/mol}} + \frac{(100 - C_V)}{55.85 \text{ g/mol}}}$$

whereas for ρ_{ave}

$$\rho_{ave} = \frac{100}{\frac{C_V}{\rho_V} + \frac{(100 - C_V)}{\rho_{Fe}}}$$

$$= \frac{100}{\frac{C_V}{6.10 \text{ g/cm}^3} + \frac{(100 - C_V)}{7.87 \text{ g/cm}^3}}$$

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Within the BCC unit cell there are 2 equivalent atoms, and thus, the value of n in Equation 3.5 is 2; hence, this expression may be written in terms of the concentration of V in weight percent as follows:

$$V_C = 2.414 \times 10^{-23}\ \text{cm}^3$$

$$= \frac{nA_{\text{ave}}}{\rho_{\text{ave}} N_A}$$

$$= \frac{(2\ \text{atoms/unit cell})\left[\dfrac{100}{\dfrac{C_V}{50.94\ \text{g/mol}} + \dfrac{(100 - C_V)}{55.85\ \text{g/mol}}}\right]}{\left[\dfrac{100}{\dfrac{C_V}{6.10\ \text{g/cm}^3} + \dfrac{(100 - C_V)}{7.87\ \text{g/cm}^3}}\right](6.022 \times 10^{23}\ \text{atoms/mol})}$$

And solving this expression for C_V leads to C_V = 12.9 wt%.

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CHAPTER 5

DIFFUSION

PROBLEM SOLUTIONS

Introduction

5.1 *Briefly explain the difference between self-diffusion and interdiffusion.*

Solution

Self-diffusion is atomic migration in pure metals--i.e., when all atoms exchanging positions are of the same type. Interdiffusion is diffusion of atoms of one metal into another metal.

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5.2 *Self-diffusion involves the motion of atoms that are all of the same type; therefore it is not subject to observation by compositional changes, as with interdiffusion. Suggest one way in which self-diffusion may be monitored.*

Solution

Self-diffusion may be monitored by using radioactive isotopes of the metal being studied. The motion of these isotopic atoms may be monitored by measurement of radioactivity level.

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Diffusion Mechanisms

5.3 *(a) Compare interstitial and vacancy atomic mechanisms for diffusion.*

(b) Cite two reasons why interstitial diffusion is normally more rapid than vacancy diffusion.

Solution

(a) With vacancy diffusion, atomic motion is from one lattice site to an adjacent vacancy. Self-diffusion and the diffusion of substitutional impurities proceed via this mechanism. On the other hand, atomic motion is from interstitial site to adjacent interstitial site for the interstitial diffusion mechanism.

(b) Interstitial diffusion is normally more rapid than vacancy diffusion because: (1) interstitial atoms, being smaller, are more mobile; and (2) the probability of an empty adjacent interstitial site is greater than for a vacancy adjacent to a host (or substitutional impurity) atom.

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Steady-State Diffusion

5.4 *Briefly explain the concept of steady state as it applies to diffusion.*

Solution

Steady-state diffusion is the situation wherein the rate of diffusion into a given system is just equal to the rate of diffusion out, such that there is no net accumulation or depletion of diffusing species--i.e., the diffusion flux is independent of time.

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5.5 *(a) Briefly explain the concept of a driving force.*

(b) What is the driving force for steady-state diffusion?

Solution

(a) The driving force is that which compels a reaction to occur.

(b) The driving force for steady-state diffusion is the concentration gradient.

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5.6 *The purification of hydrogen gas by diffusion through a palladium sheet was discussed in Section 5.3. Compute the number of kilograms of hydrogen that pass per hour through a 5-mm-thick sheet of palladium having an area of 0.20 m^2 at 500°C. Assume a diffusion coefficient of 1.0 × 10^{-8} m^2/s, that the concentrations at the high- and low-pressure sides of the plate are 2.4 and 0.6 kg of hydrogen per cubic meter of palladium, and that steady-state conditions have been attained.*

Solution

This problem calls for the mass of hydrogen, per hour, that diffuses through a Pd sheet. It first becomes necessary to employ both Equations 5.1a and 5.3. Combining these expressions and solving for the mass yields

$$M = JAt = -DAt\frac{\Delta C}{\Delta x}$$

$$= -\left(1.0 \times 10^{-8}\ \text{m}^2/\text{s}\right)\left(0.20\ \text{m}^2\right)(3600\ \text{s/h})\left[\frac{0.6 - 2.4\ \text{kg/m}^3}{5 \times 10^{-3}\ \text{m}}\right]$$

$$= 2.6 \times 10^{-3}\ \text{kg/h}$$

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5.7 *A sheet of steel 1.5 mm thick has nitrogen atmospheres on both sides at 1200°C and is permitted to achieve a steady-state diffusion condition. The diffusion coefficient for nitrogen in steel at this temperature is* 6×10^{-11} m^2/s, *and the diffusion flux is found to be* 1.2×10^{-7} kg/m^2-*s. Also, it is known that the concentration of nitrogen in the steel at the high-pressure surface is 4* kg/m^3. *How far into the sheet from this high-pressure side will the concentration be 2.0* kg/m^3? *Assume a linear concentration profile.*

Solution

This problem is solved by using Equation 5.3 in the form

$$J = -D\frac{C_A - C_B}{x_A - x_B}$$

If we take C_A to be the point at which the concentration of nitrogen is 4 kg/m^3, then it becomes necessary to solve for x_B, as

$$x_B = x_A + D\left[\frac{C_A - C_B}{J}\right]$$

Assume x_A is zero at the surface, in which case

$$x_B = 0 + \left(6 \times 10^{-11}\ m^2/s\right)\left[\frac{4\ kg/m^3 - 2\ kg/m^3}{1.2 \times 10^{-7}\ kg/m^2\text{-}s}\right]$$

$$= 1 \times 10^{-3}\ m = 1\ mm$$

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5.8 *A sheet of BCC iron 1 mm thick was exposed to a carburizing gas atmosphere on one side and a decarburizing atmosphere on the other side at 725°C. After having reached steady state, the iron was quickly cooled to room temperature. The carbon concentrations at the two surfaces of the sheet were determined to be 0.012 and 0.0075 wt%. Compute the diffusion coefficient if the diffusion flux is 1.4 × 10^{-8} kg/m^2-s. Hint: Use Equation 4.9 to convert the concentrations from weight percent to kilograms of carbon per cubic meter of iron.*

Solution

Let us first convert the carbon concentrations from weight percent to kilograms carbon per meter cubed using Equation 4.9a. For 0.012 wt% C

$$C_C'' = \frac{C_C}{\frac{C_C}{\rho_C} + \frac{C_{Fe}}{\rho_{Fe}}} \times 10^3$$

$$= \frac{0.012}{\frac{0.012}{2.25\ \text{g/cm}^3} + \frac{99.988}{7.87\ \text{g/cm}^3}} \times 10^3$$

$$0.944\ \text{kg C/m}^3$$

Similarly, for 0.0075 wt% C

$$C_C'' = \frac{0.0075}{\frac{0.0075}{2.25\ \text{g/cm}^3} + \frac{99.9925}{7.87\ \text{g/cm}^3}} \times 10^3$$

$$= 0.590\ \text{kg C/m}^3$$

Now, using a rearranged form of Equation 5.3

$$D = -J\left[\frac{x_A - x_B}{C_A - C_B}\right]$$

$$= -\left(1.40 \times 10^{-8}\ \text{kg/m}^2\text{-s}\right)\left[\frac{-10^{-3}\ \text{m}}{0.944\ \text{kg/m}^3 - 0.590\ \text{kg/m}^3}\right]$$

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$$= 3.95 \times 10^{-11}\ m^2/s$$

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5.9 *When α-iron is subjected to an atmosphere of hydrogen gas, the concentration of hydrogen in the iron, C_H (in weight percent), is a function of hydrogen pressure, p_{H_2} (in MPa), and absolute temperature (T) according to*

$$C_{\mathrm{H}} = 1.34 \times 10^{-2} \sqrt{p_{\mathrm{H}_2}} \exp\left(-\frac{27.2 \text{ kJ/mol}}{RT}\right) \qquad (5.14)$$

Furthermore, the values of D_0 and Q_d for this diffusion system are 1.4×10^{-7} m^2/s and 13,400 J/mol, respectively. Consider a thin iron membrane 1 mm thick that is at 250°C. Compute the diffusion flux through this membrane if the hydrogen pressure on one side of the membrane is 0.15 MPa (1.48 atm), and on the other side 7.5 MPa (74 atm).

Solution

Ultimately we will employ Equation 5.3 to solve this problem. However, it first becomes necessary to determine the concentration of hydrogen at each face using Equation 5.14. At the low pressure (or B) side

$$C_{\mathrm{H(B)}} = \left(1.34 \times 10^{-2}\right)\sqrt{0.15 \text{ MPa}} \exp\left[-\frac{27{,}200 \text{ J/mol}}{(8.31 \text{ J/mol-K})(250 + 273 \text{ K})}\right]$$

$$9.93 \times 10^{-6} \text{ wt\%}$$

Whereas, for the high pressure (or A) side

$$C_{\mathrm{H(A)}} = \left(1.34 \times 10^{-2}\right)\sqrt{7.5 \text{ MPa}} \exp\left[-\frac{27{,}200 \text{ J/mol}}{(8.31 \text{ J/mol-K})(250 + 273 \text{ K})}\right]$$

$$7.02 \times 10^{-5} \text{ wt\%}$$

We now convert concentrations in weight percent to mass of nitrogen per unit volume of solid. At face B there are 9.93×10^{-6} g (or 9.93×10^{-9} kg) of hydrogen in 100 g of Fe, which is virtually pure iron. From the density of iron (7.87 g/cm^3), the volume iron in 100 g (V_{B}) is just

$$V_{\mathrm{B}} = \frac{100 \text{ g}}{7.87 \text{ g/cm}^3} = 12.7 \text{ cm}^3 = 1.27 \times 10^{-5} \text{ m}^3$$

Therefore, the concentration of hydrogen at the B face in kilograms of H per cubic meter of alloy [$C''_{\mathrm{H(B)}}$] is just

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$$C''_{H(B)} = \frac{C_{H(B)}}{V_B}$$

$$= \frac{9.93 \times 10^{-9}\ \text{kg}}{1.27 \times 10^{-5}\ \text{m}^3} = 7.82 \times 10^{-4}\ \text{kg/m}^3$$

At the A face the volume of iron in 100 g (V_A) will also be 1.27×10^{-5} m^3, and

$$C''_{H(A)} = \frac{C_{H(A)}}{V_A}$$

$$= \frac{7.02 \times 10^{-8}\ \text{kg}}{1.27 \times 10^{-5}\ \text{m}^3} = 5.53 \times 10^{-3}\ \text{kg/m}^3$$

Thus, the concentration gradient is just the difference between these concentrations of nitrogen divided by the thickness of the iron membrane; that is

$$\frac{\Delta C}{\Delta x} = \frac{C''_{H(B)} - C''_{H(A)}}{x_B - x_A}$$

$$= \frac{7.82 \times 10^{-4}\ \text{kg/m}^3 - 5.53 \times 10^{-3}\ \text{kg/m}^3}{10^{-3}\ \text{m}} = -4.75\ \text{kg/m}^4$$

At this time it becomes necessary to calculate the value of the diffusion coefficient at 250°C using Equation 5.8. Thus,

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$$= \left(1.4 \times 10^{-7}\ \text{m}^2/\text{s}\right) \exp\left(-\frac{13{,}400\ \text{J/mol}}{(8.31\ \text{J/mol-K})(250 + 273\ \text{K})}\right)$$

$$= 6.41 \times 10^{-9}\ \text{m}^2/\text{s}$$

And, finally, the diffusion flux is computed using Equation 5.3 by taking the negative product of this diffusion coefficient and the concentration gradient, as

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$$J = -D\frac{\Delta C}{\Delta x}$$

$$= -\left(6.41 \times 10^{-9}\ \text{m}^2/\text{s}\right)\left(-4.75\ \text{kg/m}^4\right) = 3.05 \times 10^{-8}\ \text{kg/m}^2\text{-s}$$

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Nonsteady-State Diffusion

5.10 *Show that*

$$C_x = \frac{B}{\sqrt{Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

is also a solution to Equation 5.4b. The parameter B is a constant, being independent of both x and t.

Solution

It can be shown that

$$C_x = \frac{B}{\sqrt{Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

is a solution to

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

simply by taking appropriate derivatives of the C_x expression. When this is carried out,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} = \frac{B}{2D^{1/2}t^{3/2}}\left(\frac{x^2}{2Dt} - 1\right)\exp\left(-\frac{x^2}{4Dt}\right)$$

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5.11 *Determine the carburizing time necessary to achieve a carbon concentration of 0.45 wt% at a position 2 mm into an iron–carbon alloy that initially contains 0.20 wt% C. The surface concentration is to be maintained at 1.30 wt% C, and the treatment is to be conducted at 1000°C. Use the diffusion data for γ-Fe in Table 5.2.*

Solution

In order to solve this problem it is first necessary to use Equation 5.5:

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

wherein, $C_x = 0.45$, $C_0 = 0.20$, $C_s = 1.30$, and $x = 2$ mm $= 2 \times 10^{-3}$ m. Thus,

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.45 - 0.20}{1.30 - 0.20} = 0.2273 = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

or

$$\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 1 - 0.2273 = 0.7727$$

By linear interpolation using data from Table 5.1

z	erf(z)
0.85	0.7707
z	0.7727
0.90	0.7970

$$\frac{z - 0.850}{0.900 - 0.850} = \frac{0.7727 - 0.7707}{0.7970 - 0.7707}$$

From which

$$z = 0.854 = \frac{x}{2\sqrt{Dt}}$$

Now, from Table 5.2, at 1000°C (1273 K)

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$$D = \left(2.3 \times 10^{-5}\ \text{m}^2/\text{s}\right) \exp\left[-\frac{148{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1273\ \text{K})}\right]$$

$$= 1.93 \times 10^{-11}\ \text{m}^2/\text{s}$$

Thus,

$$0.854 = \frac{2 \times 10^{-3}\ \text{m}}{(2)\sqrt{\left(1.93 \times 10^{-11}\ \text{m}^2/\text{s}\right)(t)}}$$

Solving for t yields

$$t = 7.1 \times 10^4\ \text{s} = 19.7\ \text{h}$$

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5.12 *An FCC iron-carbon alloy initially containing 0.35 wt% C is exposed to an oxygen-rich and virtually carbon-free atmosphere at 1400 K (1127°C). Under these circumstances the carbon diffuses from the alloy and reacts at the surface with the oxygen in the atmosphere; that is, the carbon concentration at the surface position is maintained essentially at 0 wt% C. (This process of carbon depletion is termed* decarburization*.) At what position will the carbon concentration be 0.15 wt% after a 10-h treatment? The value of D at 1400 K is* 6.9×10^{-11} m^2/s.

Solution

This problem asks that we determine the position at which the carbon concentration is 0.15 wt% after a 10-h heat treatment at 1325 K when $C_0 = 0.35$ wt% C. From Equation 5.5

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.15 - 0.35}{0 - 0.35} = 0.5714 = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Thus,

$$\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.4286$$

Using data in Table 5.1 and linear interpolation

z	erf (z)
0.40	0.4284
z	0.4286
0.45	0.4755

$$\frac{z - 0.40}{0.45 - 0.40} = \frac{0.4286 - 0.4284}{0.4755 - 0.4284}$$

And,

$$z = 0.4002$$

Which means that

$$\frac{x}{2\sqrt{Dt}} = 0.4002$$

And, finally

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$$x = 2(0.4002)\sqrt{Dt} = (0.8004)\sqrt{\left(6.9 \times 10^{-11}\ \text{m}^2/\text{s}\right)\left(3.6 \times 10^{4}\ \text{s}\right)}$$

$$= 1.26 \times 10^{-3}\ \text{m} = 1.26\ \text{mm}$$

Note: this problem may also be solved using the "Diffusion" module in the *VMSE* software. Open the "Diffusion" module, click on the "Diffusion Design" submodule, and then do the following:

1. Enter the given data in left-hand window that appears. In the window below the label "D Value" enter the value of the diffusion coefficient—viz. "6.9e-11".

2. In the window just below the label "Initial, C0" enter the initial concentration—viz. "0.35".

3. In the window the lies below "Surface, Cs" enter the surface concentration—viz. "0".

4. Then in the "Diffusion Time t" window enter the time in seconds; in 10 h there are (60 s/min)(60 min/h)(10 h) = 36,000 s—so enter the value "3.6e4".

5. Next, at the bottom of this window click on the button labeled "Add curve".

6. On the right portion of the screen will appear a concentration profile for this particular diffusion situation. A diamond-shaped cursor will appear at the upper left-hand corner of the resulting curve. Click and drag this cursor down the curve to the point at which the number below "Concentration:" reads "0.15 wt%". Then read the value under the "Distance:". For this problem, this value (the solution to the problem) is ranges between 1.24 and 1.30 mm.

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5.13 *Nitrogen from a gaseous phase is to be diffused into pure iron at 700°C. If the surface concentration is maintained at 0.1 wt% N, what will be the concentration 1 mm from the surface after 10 h? The diffusion coefficient for nitrogen in iron at 700°C is* $2.5 \times 10^{-11}\ m^2/s$.

Solution

This problem asks us to compute the nitrogen concentration (C_x) at the 1 mm position after a 10 h diffusion time, when diffusion is nonsteady-state. From Equation 5.5

$$\frac{C_x - C_0}{C_s - C_0} = \frac{C_x - 0}{0.1 - 0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$= 1 - \text{erf}\left[\frac{10^{-3}\ \text{m}}{(2)\sqrt{(2.5 \times 10^{-11}\ \text{m}^2/\text{s})(10\ \text{h})(3600\ \text{s/h})}}\right]$$

$$= 1 - \text{erf}\,(0.527)$$

Using data in Table 5.1 and linear interpolation

z	erf (z)
0.500	0.5205
0.527	y
0.550	0.5633

$$\frac{0.527 - 0.500}{0.550 - 0.500} = \frac{y - 0.5205}{0.5633 - 0.5205}$$

from which

$$y = \text{erf}\,(0.527) = 0.5436$$

Thus,

$$\frac{C_x - 0}{0.1 - 0} = 1.0 - 0.5436$$

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This expression gives

$$C_x = 0.046 \text{ wt\% N}$$

Note: this problem may also be solved using the "Diffusion" module in the *VMSE* software. Open the "Diffusion" module, click on the "Diffusion Design" submodule, and then do the following:

1. Enter the given data in left-hand window that appears. In the window below the label "D Value" enter the value of the diffusion coefficient—viz. "2.5e-11".

2. In the window just below the label "Initial, C0" enter the initial concentration—viz. "0".

3. In the window the lies below "Surface, Cs" enter the surface concentration—viz. "0.1".

4. Then in the "Diffusion Time t" window enter the time in seconds; in 10 h there are (60 s/min)(60 min/h)(10 h) = 36,000 s—so enter the value "3.6e4".

5. Next, at the bottom of this window click on the button labeled "Add curve".

6. On the right portion of the screen will appear a concentration profile for this particular diffusion situation. A diamond-shaped cursor will appear at the upper left-hand corner of the resulting curve. Click and drag this cursor down the curve to the point at which the number below "Distance:" reads "1.00 mm". Then read the value under the "Concentration:". For this problem, this value (the solution to the problem) is 0.05 wt%.

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5.14 *Consider a diffusion couple composed of two semi-infinite solids of the same metal, and that each side of the diffusion couple has a different concentration of the same elemental impurity; furthermore, assume each impurity level is constant throughout its side of the diffusion couple. For this situation, the solution to Fick's second law (assuming that the diffusion coefficient for the impurity is independent of concentration), is as follows:*

$$C_x = \left(\frac{C_1 + C_2}{2}\right) - \left(\frac{C_1 - C_2}{2}\right)\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (5.15)$$

In this expression, when the x = 0 position is taken as the initial diffusion couple interface, then C_1 is the impurity concentration for x < 0; likewise, C_2 is the impurity content for x > 0.

A diffusion couple composed of two silver-gold alloys is formed; these alloys have compositions of 98 wt% Ag–2 wt% Au and 95 wt% Ag–5 wt% Au. Determine the time this diffusion couple must be heated at 750ºC (1023 K) in order for the composition to be 2.5 wt% Au at the 50 μm position into the 2 wt% Au side of the diffusion couple. Preexponential and activation energy values for Au diffusion in Ag are 8.5 × 10^{-5} m^2/s and 202,100 J/mol, respectively.

Solution

For this platinum-gold diffusion couple for which C_1 = 5 wt% Au and C_2 = 2 wt% Au, we are asked to determine the diffusion time at 750°C that will give a composition of 2.5 wt% Au at the 50 μm position. Thus, for this problem, Equation 5.15 takes the form

$$2.5 = \left(\frac{5 + 2}{2}\right) - \left(\frac{5 - 2}{2}\right)\text{erf}\left(\frac{50 \times 10^{-6}\ \text{m}}{2\sqrt{Dt}}\right)$$

It now becomes necessary to compute the diffusion coefficient at 750°C (1023 K) given that D_0 = 8.5 × 10^{-5} m^2/s and Q_d = 202,100 J/mol. From Equation 5.8 we have

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$$= \left(8.5 \times 10^{-5}\ \text{m}^2/\text{s}\right) \exp\left[-\frac{202{,}100\ \text{J/mol}}{(8.31\ \text{J/mol} - \text{K})(1023\ \text{K})}\right]$$

$$= 4.03 \times 10^{-15}\ \text{m}^2/\text{s}$$

Substitution of this value into the above equation leads to

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$$2.5 = \left(\frac{5 + 2}{2}\right) - \left(\frac{5 - 2}{2}\right) \text{erf}\left[\frac{50 \times 10^{-6} \text{ m}}{2\sqrt{(4.03 \times 10^{-15} \text{ m}^2/\text{s})(t)}}\right]$$

This expression reduces to the following form:

$$0.6667 = \text{erf}\left(\frac{393.8\sqrt{\text{s}}}{\sqrt{t}}\right)$$

Using data in Table 5.1, it is necessary to determine the value of z for which the error function is 0.6667 We use linear interpolation as follows:

z	erf (z)
0.650	0.6420
y	0.6667
0.700	0.6778

$$\frac{y - 0.650}{0.700 - 0.650} = \frac{0.6667 - 0.6420}{0.6778 - 0.6420}$$

from which

$$y = 0.6844 = \frac{393.8\sqrt{\text{s}}}{\sqrt{t}}$$

And, solving for t gives

$$t = 3.31 \times 10^5 \text{ s} = 92 \text{ h}$$

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5.15 *For a steel alloy it has been determined that a carburizing heat treatment of 10-h duration will raise the carbon concentration to 0.45 wt% at a point 2.5 mm from the surface. Estimate the time necessary to achieve the same concentration at a 5.0-mm position for an identical steel and at the same carburizing temperature.*

Solution

This problem calls for an estimate of the time necessary to achieve a carbon concentration of 0.45 wt% at a point 5.0 mm from the surface. From Equation 5.6b,

$$\frac{x^2}{Dt} = \text{constant}$$

But since the temperature is constant, so also is D constant, and

$$\frac{x^2}{t} = \text{constant}$$

or

$$\frac{x_1^2}{t_1} = \frac{x_2^2}{t_2}$$

Thus,

$$\frac{(2.5\text{ mm})^2}{10\text{ h}} = \frac{(5.0\text{ mm})^2}{t_2}$$

from which

$$t_2 = 40\text{ h}$$

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Factors That Influence Diffusion

5.16 *Cite the values of the diffusion coefficients for the interdiffusion of carbon in both α-iron (BCC) and γ-iron (FCC) at 900°C. Which is larger? Explain why this is the case.*

Solution

We are asked to compute the diffusion coefficients of C in both α and γ iron at 900°C. Using the data in Table 5.2,

$$D_\alpha = \left(6.2 \times 10^{-7}\ \text{m}^2/\text{s}\right) \exp\left[-\frac{80{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1173\ \text{K})}\right]$$

$$= 1.69 \times 10^{-10}\ \text{m}^2/\text{s}$$

$$D_\gamma = \left(2.3 \times 10^{-5}\ \text{m}^2/\text{s}\right) \exp\left[-\frac{148{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1173\ \text{K})}\right]$$

$$= 5.86 \times 10^{-12}\ \text{m}^2/\text{s}$$

The D for diffusion of C in BCC α iron is larger, the reason being that the atomic packing factor is smaller than for FCC γ iron (0.68 versus 0.74—Section 3.4); this means that there is slightly more interstitial void space in the BCC Fe, and, therefore, the motion of the interstitial carbon atoms occurs more easily.

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5.17 *Using the data in Table 5.2, compute the value of D for the diffusion of zinc in copper at 650ºC.*

Solution

Incorporating the appropriate data from Table 5.2 into Equation 5.8 leads to

$$D = \left(2.4 \times 10^{-5}\ \text{m}^2/\text{s}\right) \exp\left[-\frac{189{,}000\ \text{J/mol}}{(8.31\ \text{J/mol - K})(650 + 273\ \text{K})}\right]$$

$$= 4.8 \times 10^{-16}\ \text{m}^2/\text{s}$$

Note: this problem may also be solved using the "Diffusion" module in the *VMSE* software. Open the "Diffusion" module, click on the "D vs 1/T Plot" submodule, and then do the following:

1. In the left-hand window that appears, click on the "Zn-Cu" pair under the "Diffusing Species"-"Host Metal" headings.

2. Next, at the bottom of this window, click the "Add Curve" button.

3. A log D versus 1/T plot then appears, with a line for the temperature dependence of the diffusion coefficient for Zn in Cu. Now under "Temp Range" in the boxes appearing below "T Max" change the temperature to either "650" C or "923" K. At the top of this curve is a diamond-shaped cursor. Click-and-drag this cursor down the line to the point at which the entry under the "Temperature (T):" label reads 923 K (inasmuch as this is the Kelvin equivalent of 650ºC). Finally, the diffusion coefficient value at this temperature is given under the label "Diff Coeff (D):". For this problem, the value is $4.7 \times 10^{-16}\ \text{m}^2/\text{s}$.

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5.18 *At what temperature will the diffusion coefficient for the diffusion of copper in nickel have a value of* 6.5×10^{-17} m^2/s. *Use the diffusion data in Table 5.2.*

Solution

Solving for T from Equation 5.9a

$$T = -\frac{Q_d}{R(\ln D - \ln D_0)}$$

and using the data from Table 5.2 for the diffusion of Cu in Ni (i.e., $D_0 = 2.7 \times 10^{-5}$ m^2/s and $Q_d = 256{,}000$ J/mol) , we get

$$T = -\frac{256{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})\left[\ln\left(6.5 \times 10^{-17} \text{ m}^2/\text{s}\right) - \ln\left(2.7 \times 10^{-5} \text{ m}^2/\text{s}\right)\right]}$$

$$= 1152 \text{ K} = 879°\text{C}$$

Note: this problem may also be solved using the "Diffusion" module in the *VMSE* software. Open the "Diffusion" module, click on the "D vs 1/T Plot" submodule, and then do the following:

1. In the left-hand window that appears, there is a preset set of data for several diffusion systems. Click on the box for which Cu is the diffusing species and Ni is the host metal. Next, at the bottom of this window, click the "Add Curve" button.

2. A log D versus 1/T plot then appears, with a line for the temperature dependence of the diffusion coefficient for Cu in Ni. At the top of this curve is a diamond-shaped cursor. Click-and-drag this cursor down the line to the point at which the entry under the "Diff Coeff (D):" label reads 6.5×10^{-17} m^2/s. The temperature at which the diffusion coefficient has this value is given under the label "Temperature (T):". For this problem, the value is 1153 K.

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5.19 *The preexponential and activation energy for the diffusion of iron in cobalt are 1.1 × 10^{-5} m^2/s and 253,300 J/mol, respectively. At what temperature will the diffusion coefficient have a value of 2.1 × 10^{-14} m^2/s?*

Solution

For this problem we are given D_0 (1.1×10^{-5}) and Q_d (253,300 J/mol) for the diffusion of Fe in Co, and asked to compute the temperature at which $D = 2.1 \times 10^{-14}$ m^2/s. Solving for T from Equation 5.9a yields

$$T = \frac{Q_d}{R(\ln D_0 - \ln D)}$$

$$= \frac{253{,}300 \text{ J/mol}}{(8.31 \text{ J/mol - K})\left[\ln\left(1.1 \times 10^{-5} \text{ m}^2/\text{s}\right) - \ln\left(2.1 \times 10^{-14} \text{ m}^2/\text{s}\right)\right]}$$

$$= 1518 \text{ K} = 1245°\text{C}$$

Note: this problem may also be solved using the "Diffusion" module in the *VMSE* software. Open the "Diffusion" module, click on the "D vs 1/T Plot" submodule, and then do the following:

1. In the left-hand window that appears, click on the "Custom1" box.

2. In the column on the right-hand side of this window enter the data for this problem. In the window under "D0" enter preexponential value—viz. "1.1e-5". Next just below the "Qd" window enter the activation energy value—viz. "253.3". It is next necessary to specify a temperature range over which the data is to be plotted. The temperature at which *D* has the stipulated value is probably between 1000ºC and 1500ºC, so enter "1000" in the "T Min" box that is beside "C"; and similarly for the maximum temperature—enter "1500" in the box below "T Max".

3. Next, at the bottom of this window, click the "Add Curve" button.

4. A log D versus 1/T plot then appears, with a line for the temperature dependence of the diffusion coefficient for Fe in Co. At the top of this curve is a diamond-shaped cursor. Click-and-drag this cursor down the line to the point at which the entry under the "Diff Coeff (D):" label reads 2.1×10^{-14} m^2/s. The temperature at which the diffusion coefficient has this value is given under the label "Temperature (T):". For this problem, the value is 1519 K.

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5.20 *The activation energy for the diffusion of carbon in chromium is 111,000 J/mol. Calculate the diffusion coefficient at 1100 K (827°C), given that D at 1400 K (1127°C) is 6.25 × 10^{-11} m^2/s.*

Solution

To solve this problem it first becomes necessary to solve for D_0 from Equation 5.8 as

$$D_0 = D \exp\left(\frac{Q_d}{RT}\right)$$

$$= \left(6.25 \times 10^{-11}\ \text{m}^2/\text{s}\right)\exp\left[\frac{111{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1400\ \text{K})}\right]$$

$$= 8.7 \times 10^{-7}\ \text{m}^2/\text{s}$$

Now, solving for D at 1100 K (again using Equation 5.8) gives

$$D = \left(8.7 \times 10^{-7}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{111{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1100\ \text{K})}\right]$$

$$= 4.6 \times 10^{-12}\ \text{m}^2/\text{s}$$

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5.21 *The diffusion coefficients for iron in nickel are given at two temperatures:*

T (K)	D (m^2/s)
1273	9.4×10^{-16}
1473	2.4×10^{-14}

(a) Determine the values of D_0 and the activation energy Q_d.

(b) What is the magnitude of D at 1100°C (1373 K)?

Solution

(a) Using Equation 5.9a, we set up two simultaneous equations with Q_d and D_0 as unknowns as follows:

$$\ln D_1 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_1}\right)$$

$$\ln D_2 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_2}\right)$$

Now, solving for Q_d in terms of temperatures T_1 and T_2 (1273 K and 1473 K) and D_1 and D_2 (9.4×10^{-16} and 2.4×10^{-14} m^2/s), we get

$$Q_d = -R\,\frac{\ln D_1 - \ln D_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$$= -(8.31\ \text{J/mol-K})\,\frac{\left[\ln\left(9.4 \times 10^{-16}\right) - \ln\left(2.4 \times 10^{-14}\right)\right]}{\frac{1}{1273\ \text{K}} - \frac{1}{1473\ \text{K}}}$$

$$= 252{,}400\ \text{J/mol}$$

Now, solving for D_0 from Equation 5.8 (and using the 1273 K value of D)

$$D_0 = D_1 \exp\left(\frac{Q_d}{RT_1}\right)$$

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$$= \left(9.4 \times 10^{-16}\ \text{m}^2/\text{s}\right)\exp\left[\frac{252{,}400\ \text{J/mol}}{(8.31\ \text{J/mol - K})(1273\ \text{K})}\right]$$

$$= 2.2 \times 10^{-5}\ \text{m}^2/\text{s}$$

(b) Using these values of D_0 and Q_d, D at 1373 K is just

$$D = \left(2.2 \times 10^{-5}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{252{,}400\ \text{J/mol}}{(8.31\ \text{J/mol - K})(1373\ \text{K})}\right]$$

$$= 5.4 \times 10^{-15}\ \text{m}^2/\text{s}$$

Note: this problem may also be solved using the "Diffusion" module in the *VMSE* software. Open the "Diffusion" module, click on the "D0 and Qd from Experimental Data" submodule, and then do the following:

1. In the left-hand window that appears, enter the two temperatures from the table in the book (viz. "1273" and "1473", in the first two boxes under the column labeled "T (K)". Next, enter the corresponding diffusion coefficient values (viz. "9.4e-16" and "2.4e-14").

3. Next, at the bottom of this window, click the "Plot data" button.

4. A log D versus 1/T plot then appears, with a line for the temperature dependence for this diffusion system. At the top of this window are give values for D_0 and Q_d; for this specific problem these values are 2.17×10^{-5} m^2/s and 252 kJ/mol, respectively

5. To solve the (b) part of the problem we utilize the diamond-shaped cursor that is located at the top of the line on this plot. Click-and-drag this cursor down the line to the point at which the entry under the "Temperature (T):" label reads "1373". The value of the diffusion coefficient at this temperature is given under the label "Diff Coeff (D):". For our problem, this value is 5.4×10^{-15} m^2/s.

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5.22 *The diffusion coefficients for silver in copper are given at two temperatures:*

T (°C)	*D* (m^2/s)
650	5.5×10^{-16}
900	1.3×10^{-13}

(a) Determine the values of D_0 and Q_d.

(b) What is the magnitude of D at 875°C?

Solution

(a) Using Equation 5.9a, we set up two simultaneous equations with Q_d and D_0 as unknowns as follows:

$$\ln D_1 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_1}\right)$$

$$\ln D_2 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_2}\right)$$

Solving for Q_d in terms of temperatures T_1 and T_2 (923 K [650°C] and 1173 K [900°C]) and D_1 and D_2 (5.5×10^{-16} and 1.3×10^{-13} m^2/s), we get

$$Q_d = -R\,\frac{\ln D_1 - \ln D_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$$= -\frac{(8.31 \text{ J/mol-K})\left[\ln\left(5.5 \times 10^{-16}\right) - \ln\left(1.3 \times 10^{-13}\right)\right]}{\frac{1}{923 \text{ K}} - \frac{1}{1173 \text{ K}}}$$

$$= 196{,}700 \text{ J/mol}$$

Now, solving for D_0 from Equation 5.8 (and using the 650°C value of *D*)

$$D_0 = D_1 \exp\left(\frac{Q_d}{RT_1}\right)$$

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$$= \left(5.5 \times 10^{-16}\ \text{m}^2/\text{s}\right)\exp\left[\frac{196{,}700\ \text{J/mol}}{(8.31\ \text{J/mol - K})(923\ \text{K})}\right]$$

$$= 7.5 \times 10^{-5}\ \text{m}^2/\text{s}$$

(b) Using these values of D_0 and Q_d, D at 1148 K (875°C) is just

$$D = \left(7.5 \times 10^{-5}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{196{,}700\ \text{J/mol}}{(8.31\ \text{J/mol - K})(1148\ \text{K})}\right]$$

$$= 8.3 \times 10^{-14}\ \text{m}^2/\text{s}$$

Note: this problem may also be solved using the "Diffusion" module in the *VMSE* software. Open the "Diffusion" module, click on the "D0 and Qd from Experimental Data" submodule, and then do the following:

1. In the left-hand window that appears, enter the two temperatures from the table in the book (converted from degrees Celsius to Kelvins) (viz. "923" (650ºC) and "1173" (900ºC), in the first two boxes under the column labeled "T (K)". Next, enter the corresponding diffusion coefficient values (viz. "5.5e-16" and "1.3e-13").

3. Next, at the bottom of this window, click the "Plot data" button.

4. A log D versus 1/T plot then appears, with a line for the temperature dependence for this diffusion system. At the top of this window are give values for D_0 and Q_d; for this specific problem these values are 7.55×10^{-5} m^2/s and 196 kJ/mol, respectively

5. To solve the (b) part of the problem we utilize the diamond-shaped cursor that is located at the top of the line on this plot. Click-and-drag this cursor down the line to the point at which the entry under the "Temperature (T):" label reads "1148" (i.e., 875ºC). The value of the diffusion coefficient at this temperature is given under the label "Diff Coeff (D):". For our problem, this value is 8.9×10^{-14} m^2/s.

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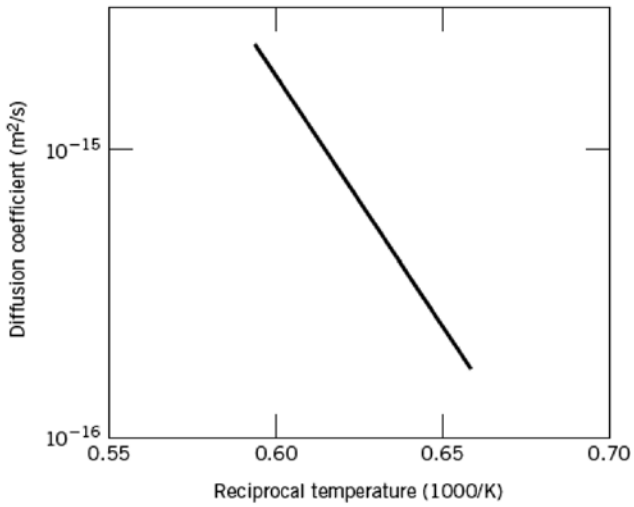
5.23 *Below is shown a plot of the logarithm (to the base 10) of the diffusion coefficient versus reciprocal of the absolute temperature, for the diffusion of iron in chromium. Determine values for the activation energy and preexponential.*



Solution

This problem asks us to determine the values of Q_d and D_0 for the diffusion of Fe in Cr from the plot of log D versus $1/T$. According to Equation 5.9b the slope of this plot is equal to $-\frac{Q_d}{2.3R}$ (rather than $-\frac{Q_d}{R}$ since we are using log D rather than ln D) and the intercept at $1/T = 0$ gives the value of log D_0. The slope is equal to

$$\text{slope} = \frac{\Delta(\log D)}{\Delta\left(\frac{1}{T}\right)} = \frac{\log D_1 - \log D_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

Taking $1/T_1$ and $1/T_2$ as 0.65×10^{-3} and 0.60×10^{-3} K^{-1}, respectively, then the corresponding values of D_1 and D_2 are 2.81×10^{-16} and 1.82×10^{-15}, as noted in the figure below.

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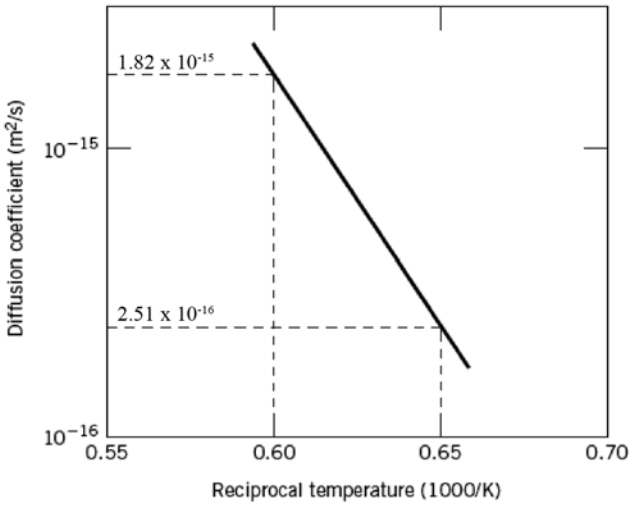

The values of log D_1 and log D_2 are –15.60 and –14.74, and therefore,

$$Q_d = -2.3\,R\,(\text{slope})$$

$$Q_d = -2.3\,R\,\frac{\log D_1 - \log D_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$$= -(2.3)(8.31\ \text{J/mol-K})\left[\frac{-15.60 - (-14.74)}{\left(0.65 \times 10^{-3} - 0.60 \times 10^{-3}\right)\ \text{K}^{-1}}\right]$$

$$= 329{,}000\ \text{J/mol}$$

Rather than trying to make a graphical extrapolation to determine D_0, a more accurate value is obtained analytically using Equation 5.9b taking a specific value of both D and T (from $1/T$) from the plot given in the problem; for example, $D = 1.0 \times 10^{-15}$ m^2/s at $T = 1626$ K ($1/T = 0.615 \times 10^{-3}$ K^{-1}). Therefore

$$D_0 = D\exp\left(\frac{Q_d}{RT}\right)$$

$$= \left(1.0 \times 10^{-15}\ \text{m}^2/\text{s}\right)\exp\left[\frac{329{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1626\ \text{K})}\right]$$

$$= 3.75 \times 10^{-5}\ \text{m}^2/\text{s}$$

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5.24 *Carbon is allowed to diffuse through a steel plate 15 mm thick. The concentrations of carbon at the two faces are 0.65 and 0.30 kg C/m^3 Fe, which are maintained constant. If the preexponential and activation energy are 6.2 $\times$ 10^{-7} m^2/s and 80,000 J/mol, respectively, compute the temperature at which the diffusion flux is 1.43 $\times$ 10^{-9} kg/m^2-s.*

Solution

Combining Equations 5.3 and 5.8 yields

$$J = -D\frac{\Delta C}{\Delta x}$$

$$= -D_0\frac{\Delta C}{\Delta x}\exp\left(-\frac{Q_d}{RT}\right)$$

Solving for T from this expression leads to

$$T = \left(\frac{Q_d}{R}\right)\frac{1}{\ln\left(-\frac{D_0\Delta C}{J\,\Delta x}\right)}$$

And incorporation of values provided in the problem statement yields

$$= \left(\frac{80{,}000\ \text{J/mol}}{8.31\ \text{J/mol - K}}\right)\frac{1}{\ln\left[\frac{(6.2\times10^{-7}\ \text{m}^2/\text{s})(0.65\ \text{kg/m}^3\ -\ 0.30\ \text{kg/m}^3)}{(1.43\times10^{-9}\ \text{kg/m}^2\text{ - s})(15\ \times\ 10^{-3}\ \text{m})}\right]}$$

$$= 1044\ \text{K} = 771°\text{C}$$

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5.25 *The steady-state diffusion flux through a metal plate is 5.4×10^{-10} kg/m^2-s at a temperature of 727°C (1000 K) and when the concentration gradient is -350 kg/m^4. Calculate the diffusion flux at 1027°C (1300 K) for the same concentration gradient and assuming an activation energy for diffusion of 125,000 J/mol.*

Solution

In order to solve this problem, we must first compute the value of D_0 from the data given at 727°C (1000 K); this requires the combining of both Equations 5.3 and 5.8 as

$$J = -D\frac{\Delta C}{\Delta x}$$

$$= -D_0\frac{\Delta C}{\Delta x}\exp\left(-\frac{Q_d}{RT}\right)$$

Solving for D_0 from the above expression gives

$$D_0 = -\frac{J}{\frac{\Delta C}{\Delta x}}\exp\left(\frac{Q_d}{RT}\right)$$

$$= -\left(\frac{5.4 \times 10^{-10}\ \text{kg/m}^2\text{-s}}{-350\ \text{kg/m}^4}\right)\exp\left[\frac{125{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1000\ \text{K})}\right]$$

$$= 5.26 \times 10^{-6}\ \text{m}^2/\text{s}$$

The value of the diffusion flux at 1300 K may be computed using these same two equations as follows:

$$J = -D_0\left(\frac{\Delta C}{\Delta x}\right)\exp\left(-\frac{Q_d}{RT}\right)$$

$$= -\left(5.26 \times 10^{-6}\ \text{m}^2/\text{s}\right)\left(-350\ \text{kg/m}^4\right)\exp\left[-\frac{125{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1300\ \text{K})}\right]$$

$$= 1.74 \times 10^{-8}\ \text{kg/m}^2\text{-s}$$

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5.26 *At approximately what temperature would a specimen of γ-iron have to be carburized for 2 h to produce the same diffusion result as at 900°C for 15 h?*

Solution

To solve this problem it is necessary to employ Equation 5.7

$$Dt = \text{constant}$$

Which, for this problem, takes the form

$$D_{900}t_{900} = D_{\text{T}}t_{\text{T}}$$

At 900°C, and using the data from Table 5.2, for the diffusion of carbon in γ-iron—i.e.,

$D_0 = 2.3 \times 10^{-5}\ \text{m}^2/\text{s}$

$Q_d = 148{,}000\ \text{J/mol}$

the diffusion coefficient is equal to

$$D_{900} = (2.3 \times 10^{-5}\ \text{m}^2/\text{s})\exp\left[-\frac{148{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(900 + 273\ \text{K})}\right]$$

$$= 5.9 \times 10^{-12}\ \text{m}^2/\text{s}$$

Thus, from the above equation

$$(5.9 \times 10^{-12}\ \text{m}^2/\text{s})(15\ \text{h}) = D_{\text{T}}(2\ \text{h})$$

And, solving for D_{T}

$$D_{\text{T}} = \frac{(5.9 \times 10^{-12}\ \text{m}^2/\text{s})(15\ \text{h})}{2\ \text{h}} = 4.43 \times 10^{-11}\ \text{m}^2/\text{s}$$

Now, solving for T from Equation 5.9a gives

$$T = -\frac{Q_d}{R(\ln D_{\text{T}} - \ln D_0)}$$

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$$= -\frac{148{,}000 \text{ J/mol}}{(8.31 \text{ J/mol - K})\left[\ln\left(4.43 \times 10^{-11} \text{ m}^2/\text{s}\right) - \ln\left(2.3 \times 10^{-5} \text{ m}^2/\text{s}\right)\right]}$$

$$= 1353 \text{ K} = 1080°\text{C}$$

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5.27 *(a) Calculate the diffusion coefficient for copper in aluminum at 500ºC.*

(b) What time will be required at 600ºC to produce the same diffusion result (in terms of concentration at a specific point) as for 10 h at 500ºC?

Solution

(a) We are asked to calculate the diffusion coefficient for Cu in Al at 500°C. Using the data in Table 5.2 and Equation 5.8

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$$= \left(6.5 \times 10^{-5}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{136{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(500 + 273\ \text{K})}\right]$$

$$= 4.15 \times 10^{-14}\ \text{m}^2/\text{s}$$

(b) This portion of the problem calls for the time required at 600°C to produce the same diffusion result as for 10 h at 500°C. Equation 5.7 is employed as

$$D_{500}t_{500} = D_{600}t_{600}$$

Now, from Equation 5.8 the value of the diffusion coefficient at 600°C is calculated as

$$D_{600} = \left(6.5 \times 10^{-5}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{136{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(600 + 273\ \text{K})}\right]$$

$$= 4.69 \times 10^{-13}\ \text{m}^2/\text{s}$$

Thus,

$$t_{600} = \frac{D_{500}t_{500}}{D_{600}}$$

$$= \frac{\left(4.15 \times 10^{-14}\ \text{m}^2/\text{s}\right)(10\,\text{h})}{\left(4.69 \times 10^{-13}\ \text{m}^2/\text{s}\right)} = 0.88\ \text{h}$$

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5.28 *A copper-nickel diffusion couple similar to that shown in Figure 5.1a is fashioned. After a 700-h heat treatment at 1100°C (1373 K) the concentration of Cu is 2.5 wt% at the 3.0-mm position within the nickel. At what temperature must the diffusion couple need to be heated to produce this same concentration (i.e., 2.5 wt% Cu) at a 2.0-mm position after 700 h? The preexponential and activation energy for the diffusion of Cu in Ni are given in Table 5.2.*

Solution

In order to determine the temperature to which the diffusion couple must be heated so as to produce a concentration of 2.5 wt% Ni at the 2.0-mm position, we must first utilize Equation 5.6b with time t being a constant. That is

$$\frac{x^2}{D} = \text{constant}$$

Or

$$\frac{x_{1100}^2}{D_{1100}} = \frac{x_T^2}{D_T}$$

Now, solving for D_T from this equation, yields

$$D_T = \frac{x_T^2 D_{1100}}{x_{1100}^2}$$

and incorporating the temperature dependence of D_{1100} utilizing Equation (5.8), realizing that for the diffusion of Cu in Ni (Table 5.2)

$D_0 = 2.7 \times 10^{-5}\ \text{m}^2/\text{s}$

$Q_d = 256{,}000\ \text{J/mol}$

then

$$D_T = \frac{\left(x_T^2\right)\left[D_0 \exp\left(-\frac{Q_d}{RT}\right)\right]}{x_{1100}^2}$$

$$= \frac{(2\ \text{mm})^2\left[\left(2.7 \times 10^{-5}\ \text{m}^2/\text{s}\right)\exp\left(-\frac{256{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1373\ \text{K})}\right)\right]}{(3\ \text{mm})^2}$$

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$$= 2.16 \times 10^{-15}\ \text{m}^2/\text{s}$$

We now need to find the T at which D has this value. This is accomplished by rearranging Equation 5.9a and solving for T as

$$T = \frac{Q_d}{R\left(\ln D_0 - \ln D\right)}$$

$$= \frac{256{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})\left[\ln\left(2.7 \times 10^{-5}\ \text{m}^2/\text{s}\right) - \ln\left(2.16 \times 10^{-15}\ \text{m}^2/\text{s}\right)\right]}$$

$$= 1325\ \text{K} = 1052°\text{C}$$

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5.29 *A diffusion couple similar to that shown in Figure 5.1a is prepared using two hypothetical metals A and B. After a 30-h heat treatment at 1000 K (and subsequently cooling to room temperature) the concentration of A in B is 3.2 wt% at the 15.5-mm position within metal B. If another heat treatment is conducted on an identical diffusion couple, only at 800 K for 30 h, at what position will the composition be 3.2 wt% A? Assume that the preexponential and activation energy for the diffusion coefficient are* 1.8×10^{-5} m^2/s *and 152,000 J/mol, respectively.*

Solution

In order to determine the position within the diffusion couple at which the concentration of A in B is 3.2 wt%, we must employ Equation 5.6b with t constant. That is

$$\frac{x^2}{D} = \text{constant}$$

Or

$$\frac{x_{800}^2}{D_{800}} = \frac{x_{1000}^2}{D_{1000}}$$

It is first necessary to compute values for both D_{800} and D_{1000}; this is accomplished using Equation 5.8 as follows:

$$D_{800} = \left(1.8 \times 10^{-5}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{152{,}000\ \text{J/mol}}{(8.31\ \text{J/mol - K})(800\ \text{K})}\right]$$

$$= 2.12 \times 10^{-15}\ \text{m}^2/\text{s}$$

$$D_{1000} = \left(1.8 \times 10^{-5}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{152{,}000\ \text{J/mol}}{(8.31\ \text{J/mol - K})(1000\ \text{K})}\right]$$

$$= 2.05 \times 10^{-13}\ \text{m}^2/\text{s}$$

Now, solving the above expression for x_{800} yields

$$x_{800} = x_{1000}\sqrt{\frac{D_{800}}{D_{1000}}}$$

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$$= (15.5 \text{ mm})\sqrt{\frac{2.12 \times 10^{-15} \text{ m}^2/\text{s}}{2.05 \times 10^{-13} \text{ m}^2/\text{s}}}$$

$$= 1.6 \text{ mm}$$

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5.30 *The outer surface of a steel gear is to be hardened by increasing its carbon content. The carbon is to be supplied from an external carbon-rich atmosphere, which is maintained at an elevated temperature. A diffusion heat treatment at 850°C (1123 K) for 10 min increases the carbon concentration to 0.90 wt% at a position 1.0 mm below the surface. Estimate the diffusion time required at 650°C (923 K) to achieve this same concentration also at a 1.0-mm position. Assume that the surface carbon content is the same for both heat treatments, which is maintained constant. Use the diffusion data in Table 5.2 for C diffusion in α-Fe.*

Solution

In order to compute the diffusion time at 650°C to produce a carbon concentration of 0.90 wt% at a position 1.0 mm below the surface we must employ Equation 5.6b with position (x) constant; that is

$$Dt = \text{constant}$$

Or

$$D_{850}t_{850} = D_{650}t_{650}$$

In addition, it is necessary to compute values for both D_{850} and D_{650} using Equation 5.8. From Table 5.2, for the diffusion of C in α-Fe, $Q_d = 80{,}000$ J/mol and $D_0 = 6.2 \times 10^{-7}$ m^2/s. Therefore,

$$D_{850} = \left(6.2 \times 10^{-7}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{80{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(850 + 273\ \text{K})}\right]$$

$$= 1.17 \times 10^{-10}\ \text{m}^2/\text{s}$$

$$D_{650} = \left(6.2 \times 10^{-7}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{80{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(650 + 273\ \text{K})}\right]$$

$$= 1.83 \times 10^{-11}\ \text{m}^2/\text{s}$$

Now, solving the original equation for t_{650} gives

$$t_{650} = \frac{D_{850}t_{850}}{D_{650}}$$

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$$= \frac{\left(1.17 \times 10^{-10}\ \mathrm{m^2/s}\right)(10\ \mathrm{min})}{1.83 \times 10^{-11}\ \mathrm{m^2/s}}$$

$$= 63.9\ \mathrm{min}$$

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5.31 *An FCC iron-carbon alloy initially containing 0.20 wt% C is carburized at an elevated temperature and in an atmosphere wherein the surface carbon concentration is maintained at 1.0 wt%. If after 49.5 h the concentration of carbon is 0.35 wt% at a position 4.0 mm below the surface, determine the temperature at which the treatment was carried out.*

Solution

This problem asks us to compute the temperature at which a nonsteady-state 49.5 h diffusion anneal was carried out in order to give a carbon concentration of 0.35 wt% C in FCC Fe at a position 4.0 mm below the surface. From Equation 5.5

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.35 - 0.20}{1.0 - 0.20} = 0.1875 = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Or

$$\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.8125$$

Now it becomes necessary, using the data in Table 5.1 and linear interpolation, to determine the value of $\frac{x}{2\sqrt{Dt}}$.

Thus

z	erf (z)
0.90	0.7970
y	0.8125
0.95	0.8209

$$\frac{y - 0.90}{0.95 - 0.90} = \frac{0.8125 - 0.7970}{0.8209 - 0.7970}$$

From which

$$y = 0.9324$$

Thus,

$$\frac{x}{2\sqrt{Dt}} = 0.9324$$

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And since t = 49.5 h (178,200 s) and x = 4.0 mm (4.0×10^{-3} m), solving for D from the above equation yields

$$D = \frac{x^2}{(4t)(0.9324)^2}$$

$$= \frac{(4.0 \times 10^{-3}\ \text{m})^2}{(4)(178,200\ \text{s})(0.869)} = 2.58 \times 10^{-11}\ \text{m}^2/\text{s}$$

Now, in order to determine the temperature at which D has the above value, we must employ Equation 5.9a; solving this equation for T yields

$$T = \frac{Q_d}{R\left(\ln D_0 - \ln D\right)}$$

From Table 5.2, D_0 and Q_d for the diffusion of C in FCC Fe are 2.3×10^{-5} m^2/s and 148,000 J/mol, respectively. Therefore

$$T = \frac{148,000\ \text{J/mol}}{(8.31\ \text{J/mol-K})\left[\ln\left(2.3 \times 10^{-5}\ \text{m}^2/\text{s}\right) - \ln\left(2.58 \times 10^{-11}\ \text{m}^2/\text{s}\right)\right]}$$

$$= 1300\ \text{K} = 1027°\text{C}$$

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Diffusion in Semiconducting Materials

5.32 *Phosphorus atoms are to be diffused into a silicon wafer using both predeposition and drive-in heat treatments; the background concentration of P in this silicon material is known to be* 5×10^{19} *atoms/m*^{3}. *The predeposition treatment is to be conducted at 950°C for 45 minutes; the surface concentration of P is to be maintained at a constant level of* 1.5×10^{26} *atoms/m*^{3}. *Drive-in diffusion will be carried out at 1200°C for a period of 2.5 h. For the diffusion of P in Si, values of* Q_d *and* D_0 *are 3.40 eV and* 1.1×10^{-4} m^2/s, *respectively.*

(a) Calculate the value of Q_0.

(b) Determine the value of x_j *for the drive-in diffusion treatment.*

(c) Also for the drive-in treatment, compute the position x at which the concentration of P atoms is 10^{24} m^{-3}.

Solution

(a) For this portion of the problem we are asked to determine the value of Q_0. This is possible using Equation 5.12. However, it is first necessary to determine the value of D for the predeposition treatment [D_p at T_p = 950°C (1223 K)] using Equation 5.8. Thus

$$D_p = D_0 \exp\left(-\frac{Q_d}{kT_p}\right)$$

$$= (1.1 \times 10^{-4}\ \text{m}^2/\text{s}) \exp\left[-\frac{3.40\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(1223\ \text{K})}\right]$$

$$= 1.08 \times 10^{-18}\ \text{m}^2/\text{s}$$

The value of Q_0 may be determined as follows:

$$Q_0 = 2C_s\sqrt{\frac{D_p t_p}{\pi}}$$

$$= (2)(1.5 \times 10^{26}\ \text{atoms/m}^3)\sqrt{\frac{(1.08 \times 10^{-18}\ \text{m}^2/\text{s})(45\ \text{min})(60\ \text{s/min})}{\pi}}$$

$$= 9.14 \times 10^{18}\ \text{atoms/m}^2$$

(b) Computation of the junction depth requires that we use Equation 5.13. However, before this is possible it is necessary to calculate D at the temperature of the drive-in treatment [D_d at 1200°C (1473 K)]. Thus,

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$$D_d = (1.1 \times 10^{-4}\ \text{m}^2/\text{s}) \exp\left[-\frac{3.40\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(1473\ \text{K})}\right]$$

$$= 2.58 \times 10^{-16}\ \text{m}^2/\text{s}$$

Now from Equation 5.13

$$x_j = \left[(4D_d t_d) \ln\left(\frac{Q_0}{C_B\sqrt{\pi D_d t_d}}\right)\right]^{1/2}$$

$$= \left\{(4)(2.58 \times 10^{-16}\ \text{m}^2/\text{s})(9000\ \text{s})\ \ln\left[\frac{9.14 \times 10^{18}\ \text{atoms/m}^2}{(5 \times 10^{19}\ \text{atoms/m}^3)\sqrt{(\pi)(2.58 \times 10^{-16}\ \text{m}^2/\text{s})(9000\ \text{s})}}\right]\right\}^{1/2}$$

$$= 1.21 \times 10^{-5}\ \text{m} = 12.1\ \mu\text{m}$$

(c) For a concentration of 10^{24} P atoms/m^3 for the drive-in treatment, we compute the value of x using Equation 5.11. However, it is first necessary to manipulate Equation 5.11 so that x is the dependent variable. Taking natural logarithms of both sides leads to

$$\ln C(x,t) = \ln\left(\frac{Q_0}{\sqrt{\pi D_d t_d}}\right) - \frac{x^2}{4D_d t_d}$$

Now, rearranging and solving for x leads to

$$x = \left\{(4D_d t_d) \ln\left[\frac{Q_0}{C(x,t)\sqrt{\pi D_d t_d}}\right]\right\}^{1/2}$$

Now, incorporating values for Q_0 and D_d determined above and taking $C(x,t) = 10^{24}$ P atoms/m^3 yields

$$x = \left\{(4)(2.58 \times 10^{-16})(9000) \ln\left[\frac{9.14 \times 10^{18}}{(10^{24})\sqrt{(\pi)(2.58 \times 10^{-16})(9000)}}\right]\right\}^{1/2}$$

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$$= 3.36 \times 10^{-6} \text{ m} = 3.36 \text{ μm}$$

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5.33 *Aluminum atoms are to be diffused into a silicon wafer using both predeposition and drive-in heat treatments; the background concentration of Al in this silicon material is known to be* 3×10^{19} *atoms/m*^{3}. *The drive-in diffusion treatment is to be carried out at 1050°C for a period of 4.0 h, which gives a junction depth* x_j *of 3.0 μm. Compute the predeposition diffusion time at 950°C if the surface concentration is maintained at a constant level of* 2×10^{25} *atoms/m*^{3}. *For the diffusion of Al in Si, values of* Q_d *and* D_0 *are 3.41 eV and* 1.38×10^{-4} m^2/s, *respectively.*`

Solution

This problem asks that we compute the time for the predeposition heat treatment for the diffusion of Al in Si. In order to do this it is necessary to determine the value of Q_0 from Equation 5.13. However, before doing this we must first calculate D_d, using Equation 5.8. Therefore

$$D_d = D_0 \exp\left(-\frac{Q_d}{kT_d}\right)$$

$$= (1.38 \times 10^{-4}\ \text{m}^2/\text{s}) \exp\left[-\frac{3.41\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(1050°\text{C} + 273\ \text{K})}\right]$$

$$= 1.43 \times 10^{-17}\ \text{m}^2/\text{s}$$

Now, solving for Q_0 in Equation 5.13 leads to

$$Q_0 = \left(C_B\sqrt{\pi D_d t_d}\right)\exp\left(\frac{x_j^2}{4D_d t_d}\right)$$

In the problem statement we are given the following values:

$C_B = 3 \times 10^{19}$ atoms/m^3

$t_d = 4$ h (14,400 s)

$x_j = 3.0\ \mu\text{m} = 3.0 \times 10^{-6}$ m

Therefore, incorporating these values into the above equation yields

$$Q_0 = \left[(3 \times 10^{19}\ \text{atoms/m}^3)\sqrt{(\pi)(1.43 \times 10^{-17}\ \text{m}^2/\text{s})(14{,}400\ \text{s})}\right]\exp\left[\frac{(3.0 \times 10^{-6}\ \text{m})^2}{(4)(1.43 \times 10^{-17}\ \text{m}^2/\text{s})(14{,}400\ \text{s})}\right]$$

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$$= 1.34 \times 10^{18} \text{ atoms/m}^2$$

We may now compute the value of t_p using Equation 5.12. However, before this is possible it is necessary to determine D_p (at 950°C) using Equation 5.8. Thus

$$D_p = (1.38 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left[-\frac{3.41 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(950°\text{C} + 273 \text{ K})}\right]$$

$$= 1.24 \times 10^{-18} \text{ m}^2/\text{s}$$

Now, solving for t_p in Equation 5.12 we get

$$t_p = \frac{\pi Q_0^2}{4C_s^2 D_p}$$

And incorporating the value of C_s provided in the problem statement (2×10^{25} atoms/m^3) as well as values for Q_0 and D_p determined above, leads to

$$t_p = \frac{\pi\left(1.34 \times 10^{18} \text{ atoms/m}^2\right)^2}{(4)\left(2 \times 10^{25} \text{ atoms/m}^3\right)^2 (1.24 \times 10^{-18} \text{ m}^2/\text{s})}$$

$$= 2.84 \times 10^3 \text{ s} = 47.4 \text{ min}$$

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DESIGN PROBLEMS

Steady-State Diffusion

5.D1 *It is desired to enrich the partial pressure of hydrogen in a hydrogen-nitrogen gas mixture for which the partial pressures of both gases are 0.1013 MPa (1 atm). It has been proposed to accomplish this by passing both gases through a thin sheet of some metal at an elevated temperature; inasmuch as hydrogen diffuses through the plate at a higher rate than does nitrogen, the partial pressure of hydrogen will be higher on the exit side of the sheet. The design calls for partial pressures of 0.0709 MPa (0.7 atm) and 0.02026 MPa (0.2 atm), respectively, for hydrogen and nitrogen. The concentrations of hydrogen and nitrogen (C_H and C_N, in mol/m^3) in this metal are functions of gas partial pressures (p_{H_2} and p_{N_2}, in MPa) and absolute temperature and are given by the following expressions:*

$$C_{\mathrm{H}} = 2.5 \times 10^{3} \sqrt{p_{\mathrm{H}_2}} \exp\left(-\frac{27.8\ \mathrm{kJ/mol}}{RT}\right) \qquad (5.16a)$$

$$C_{\mathrm{N}} = 2.75 \times 10^{-3} \sqrt{p_{\mathrm{N}_2}} \exp\left(-\frac{37.6\ \mathrm{kJ/mol}}{RT}\right) \qquad (5.16b)$$

Furthermore, the diffusion coefficients for the diffusion of these gases in this metal are functions of the absolute temperature as follows:

$$D_{\mathrm{H}}(\mathrm{m}^2/\mathrm{s}) = 1.4 \times 10^{-7} \exp\left(-\frac{13.4\ \mathrm{kJ/mol}}{RT}\right) \qquad (5.17a)$$

$$D_{\mathrm{N}}(\mathrm{m}^2/\mathrm{s}) = 3.0 \times 10^{-7} \exp\left(-\frac{76.15\ \mathrm{kJ/mol}}{RT}\right) \qquad (5.17b)$$

Is it possible to purify hydrogen gas in this manner? If so, specify a temperature at which the process may be carried out, and also the thickness of metal sheet that would be required. If this procedure is not possible, then state the reason(s) why.

Solution

This problem calls for us to ascertain whether or not a hydrogen-nitrogen gas mixture may be enriched with respect to hydrogen partial pressure by allowing the gases to diffuse through a metal sheet at an elevated temperature. If this is possible, the temperature and sheet thickness are to be specified; if such is not possible, then we are to state the reasons why. Since this situation involves steady-state diffusion, we employ Fick's first law, Equation 5.3. Inasmuch as the partial pressures on the high-pressure side of the sheet are the same, and the pressure of hydrogen on the low pressure side is 3.5 times that of nitrogen, and concentrations are proportional to the square

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root of the partial pressure, the diffusion flux of hydrogen J_H is the square root of 3.5 times the diffusion flux of nitrogen J_N--i.e.

$$J_H = \sqrt{3.5}\, J_N$$

Thus, equating the Fick's law expressions incorporating the given equations for the diffusion coefficients and concentrations in terms of partial pressures leads to the following

$$J_H$$

$$= \frac{1}{\Delta x} \times$$

$$\left(2.5 \times 10^3\right)\left(\sqrt{0.1013\ \text{MPa}} - \sqrt{0.0709\ \text{MPa}}\right)\exp\left(-\frac{27.8\ \text{kJ}}{RT}\right)\left(1.4 \times 10^{-7}\ \text{m}^2/\text{s}\right)\exp\left(-\frac{13.4\ \text{kJ}}{RT}\right)$$

$$= \sqrt{3.5}\, J_N$$

$$= \frac{\sqrt{3.5}}{\Delta x} \times$$

$$\left(2.75 \times 10^3\right)\left(\sqrt{0.1013\ \text{MPa}} - \sqrt{0.02026\ \text{MPa}}\right)\exp\left(-\frac{37.6\ \text{kJ}}{RT}\right)\left(3.0 \times 10^{-7}\ \text{m}^2/\text{s}\right)\exp\left(-\frac{76.15\ \text{kJ}}{RT}\right)$$

The Δx's cancel out, which means that the process is independent of sheet thickness. Now solving the above expression for the absolute temperature T gives

$$T = 3237\ \text{K}$$

which value is extremely high (surely above the melting point of the metal). Thus, such a diffusion process is *not possible*.

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5.D2 *A gas mixture is found to contain two diatomic A and B species for which the partial pressures of both are 0.05065 MPa (0.5 atm). This mixture is to be enriched in the partial pressure of the A species by passing both gases through a thin sheet of some metal at an elevated temperature. The resulting enriched mixture is to have a partial pressure of 0.02026 MPa (0.2 atm) for gas A, and 0.01013 MPa (0.1 atm) for gas B. The concentrations of A and B (C_A and C_B, in mol/m^3) are functions of gas partial pressures (p_{A_2} and p_{B_2}, in MPa) and absolute temperature according to the following expressions:*

$$C_{\mathrm{A}} = 200\sqrt{p_{\mathrm{A}_2}}\,\exp\left(-\frac{25.0\ \mathrm{kJ/mol}}{RT}\right) \qquad (5.18a)$$

$$C_{\mathrm{B}} = 1.0 \times 10^{-3}\sqrt{p_{\mathrm{B}_2}}\,\exp\left(-\frac{30.0\ \mathrm{kJ/mol}}{RT}\right) \qquad (5.18b)$$

Furthermore, the diffusion coefficients for the diffusion of these gases in the metal are functions of the absolute temperature as follows:

$$D_{\mathrm{A}}(\mathrm{m}^2/\mathrm{s}) = 4.0 \times 10^{-7}\exp\left(-\frac{15.0\ \mathrm{kJ/mol}}{RT}\right) \qquad (5.19a)$$

$$D_{\mathrm{B}}(\mathrm{m}^2/\mathrm{s}) = 2.5 \times 10^{-6}\exp\left(-\frac{24.0\ \mathrm{kJ/mol}}{RT}\right) \qquad (5.19b)$$

Is it possible to purify the A gas in this manner? If so, specify a temperature at which the process may be carried out, and also the thickness of metal sheet that would be required. If this procedure is not possible, then state the reason(s) why.

Solution

This problem calls for us to ascertain whether or not an A_2-B_2 gas mixture may be enriched with respect to the A partial pressure by allowing the gases to diffuse through a metal sheet at an elevated temperature. If this is possible, the temperature and sheet thickness are to be specified; if such is not possible, then we are to state the reasons why. Since this situation involves steady-state diffusion, we employ Fick's first law, Equation 5.3. Inasmuch as the partial pressures on the high-pressure side of the sheet are the same, and the pressure of A_2 on the low pressure side is 2.0 times that of B_2, and concentrations are proportional to the square root of the partial pressure, the diffusion flux of A, J_{A}, is the square root of 2.0 times the diffusion flux of nitrogen J_{B}--i.e.

$$J_{\mathrm{A}} = \sqrt{2.0}\,J_{\mathrm{B}}$$

Thus, equating the Fick's law expressions incorporating the given equations for the diffusion coefficients and concentrations in terms of partial pressures leads to the following

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$$J_{\mathrm{A}}$$

$$= \frac{1}{\Delta x} \times$$
$$(200)\left(\sqrt{0.05065\ \mathrm{MPa}} - \sqrt{0.02026\ \mathrm{MPa}}\right) \exp\left(-\frac{25.0\ \mathrm{kJ}}{RT}\right)\left(4.0 \times 10^{-7}\ \mathrm{m^2/s}\right) \exp\left(-\frac{15.0\ \mathrm{kJ}}{RT}\right)$$

$$= \sqrt{2.0}\, J_{\mathrm{B}}$$

$$= \frac{\sqrt{2.0}}{\Delta x} \times$$
$$\left(1.0 \times 10^{3}\right)\left(\sqrt{0.05065\ \mathrm{MPa}} - \sqrt{0.01013\ \mathrm{MPa}}\right) \exp\left(-\frac{30.0\ \mathrm{kJ}}{RT}\right)\left(2.5 \times 10^{-6}\ \mathrm{m^2/s}\right) \exp\left(-\frac{24.0\ \mathrm{kJ}}{RT}\right)$$

The Δx's cancel out, which means that the process is independent of sheet thickness. Now solving the above expression for the absolute temperature T gives

$$T = 401\ \mathrm{K}\ (128°\mathrm{C})$$

Thus, it is possible to carry out this procedure at 401 K or 128°C.

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Nonsteady-State Diffusion

5.D3 *The wear resistance of a steel shaft is to be improved by hardening its surface. This is to be accomplished by increasing the nitrogen content within an outer surface layer as a result of nitrogen diffusion into the steel. The nitrogen is to be supplied from an external nitrogen-rich gas at an elevated and constant temperature. The initial nitrogen content of the steel is 0.002 wt%, whereas the surface concentration is to be maintained at 0.50 wt%. For this treatment to be effective, a nitrogen content of 0.10 wt% must be established at a position 0.40 mm below the surface. Specify appropriate heat treatments in terms of temperature and time for temperatures between 475°C and 625°C. The preexponential and activation energy for the diffusion of nitrogen in iron are* 3×10^{-7} m^2/s *and 76,150 J/mol, respectively, over this temperature range.*

Solution

This is a nonsteady-state diffusion situation; thus, it is necessary to employ Equation 5.5, utilizing the following values for the concentration parameters:

$$C_0 = 0.002 \text{ wt\% N}$$
$$C_s = 0.50 \text{ wt\% N}$$
$$C_x = 0.10 \text{ wt\% N}$$

Therefore

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.10 - 0.002}{0.50 - 0.002}$$

$$= 0.1968 = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

And thus

$$1 - 0.1968 = 0.8032 = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Using linear interpolation and the data presented in Table 5.1

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z	erf (z)
0.9000	0.7970
y	0.8032
0.9500	0.8209

$$\frac{0.8032 - 0.7970}{0.8209 - 0.7970} = \frac{y - 0.9000}{0.9500 - 0.9000}$$

From which

$$y = \frac{x}{2\sqrt{Dt}} = 0.9130$$

The problem stipulates that $\boldsymbol{x} = 0.40$ mm $= 4.0 \times 10^{-4}$ m. Therefore

$$\frac{4.0 \times 10^{-4}\ \text{m}}{2\sqrt{Dt}} = 0.9130$$

Which leads to

$$Dt = 4.80 \times 10^{-8}\ \text{m}^2$$

Furthermore, the diffusion coefficient depends on temperature according to Equation 5.8; and, as stipulated in the problem statement, $D_0 = 3 \times 10^{-7}$ m^2/s and $Q_d = 76{,}150$ J/mol. Hence

$$Dt = D_0 \exp\left(-\frac{Q_d}{RT}\right)(t) = 4.80 \times 10^{-8}\ \text{m}^2$$

$$\left(3.0 \times 10^{-7}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{76{,}150\ \text{J/mol}}{(8.31\ \text{J/mol - K})(T)}\right](t) = 4.80 \times 10^{-8}\ \text{m}^2$$

And solving for the time t

$$t\ (\text{in s}) = \frac{0.160}{\exp\left(-\frac{9163.7}{T}\right)}$$

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Thus, the required diffusion time may be computed for some specified temperature (in K). Below are tabulated t values for three different temperatures that lie within the range stipulated in the problem.

Temperature (°C)	Time	
	s	h
500	22,500	6.3
550	11,000	3.1
600	5800	1.6

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Diffusion in Semiconducting Materials

5.D4 *One integrated circuit design calls for the diffusion of arsenic into silicon wafers; the background concentration of As in Si is 2.5 × 10^{20} atoms/m^3. The predeposition heat treatment is to be conducted at 1000°C for 45 minutes, with a constant surface concentration of 8 × 10^{26} As atoms/m^3. At a drive-in treatment temperature of 1100°C, determine the diffusion time required for a junction depth of 1.2 μm. For this system, values of Q_d and D_0 are 4.10 eV and 2.29 × 10^{-3} m^2/s, respectively.*

Solution

This problem asks that we compute the drive-in diffusion time for arsenic diffusion in silicon. It is first necessary to determine the value of Q_0 using Equation 5.12. But before this is possible, the value of D_p at 1000°C must be computed with the aid of Equation 5.8. Thus,

$$D_p = D_0 \exp\left(-\frac{Q_d}{kT_p}\right)$$

$$= (2.29 \times 10^{-3}\ \text{m}^2/\text{s}) \exp\left[-\frac{4.10\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(1000°\text{C} + 273\ \text{K})}\right]$$

$$= 1.36 \times 10^{-19}\ \text{m}^2/\text{s}$$

Now for the computation of Q_0 using Equation 5.12:

$$Q_0 = 2C_s\sqrt{\frac{D_p t_p}{\pi}}$$

$$= (2)(8 \times 10^{26}\ \text{atoms/m}^3)\sqrt{\frac{(1.36 \times 10^{-19}\ \text{m}^2/\text{s})(45\ \text{min})(60\ \text{s/min})}{\pi}}$$

$$= 1.73 \times 10^{19}\ \text{atoms/m}^2$$

We now desire to calculate t_d in Equation 5.13. Algebraic manipulation and rearrangement of this expression leads to

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$$\exp\left(\frac{x_j^2}{4D_d t_d}\right) = \frac{Q_0}{C_B\sqrt{\pi D_d t_d}}$$

At this point it is necessary to determine the value of D_d (at 1100°C). Thus

$$D_d = (2.29 \times 10^{-3}\ \text{m}^2/\text{s})\exp\left[-\frac{4.10\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(1100°\text{C} + 273\ \text{K})}\right]$$

$$= 2.06 \times 10^{-18}\ \text{m}^2/\text{s}$$

And incorporation of values of all parameters except t_d in the above expression yields

$$\exp\left[\frac{(1.2 \times 10^{-6}\ \text{m})^2}{(4)(2.06 \times 10^{-18}\ \text{m}^2/\text{s})t_d}\right] = \frac{1.73 \times 10^{19}\ \text{atoms/m}^2}{(2.5 \times 10^{20}\ \text{atoms/m}^3)\sqrt{(\pi)(2.06 \times 10^{-18}\ \text{m}^2/\text{s})t_d}}$$

which expression reduces to

$$\exp\left(\frac{1.75 \times 10^5\ \text{s}}{t_d}\right) = \frac{2.72 \times 10^7\ \text{s}^{1/2}}{\sqrt{t_d}}$$

Solving for t_d is not a simple matter. One possibility is to use a graphing technique. Let us take the logarithm of both sides of the above equation, which gives

$$\frac{1.75 \times 10^5\ \text{s}}{t_d} = \ln\left(\frac{2.72 \times 10^7\ \text{s}^{1/2}}{\sqrt{t_d}}\right)$$

Now if we plot the terms on both left and right hand sides of this equation versus t_d, the value of t_d at the point of intersection of the two resulting curves is correct answer. Below is such a plot:

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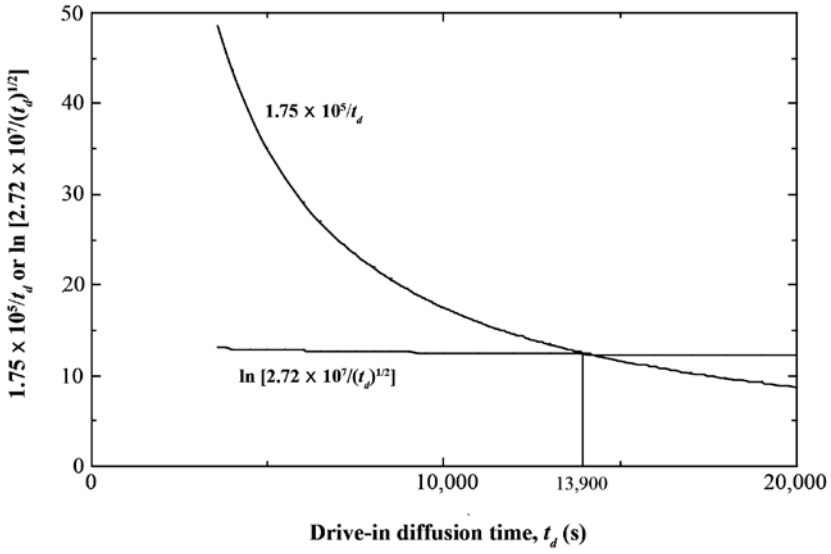

As noted, the two curves intersect at about 13,900 s, which corresponds to t_d = 3.86 h.

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CHAPTER 6

MECHANICAL PROPERTIES OF METALS

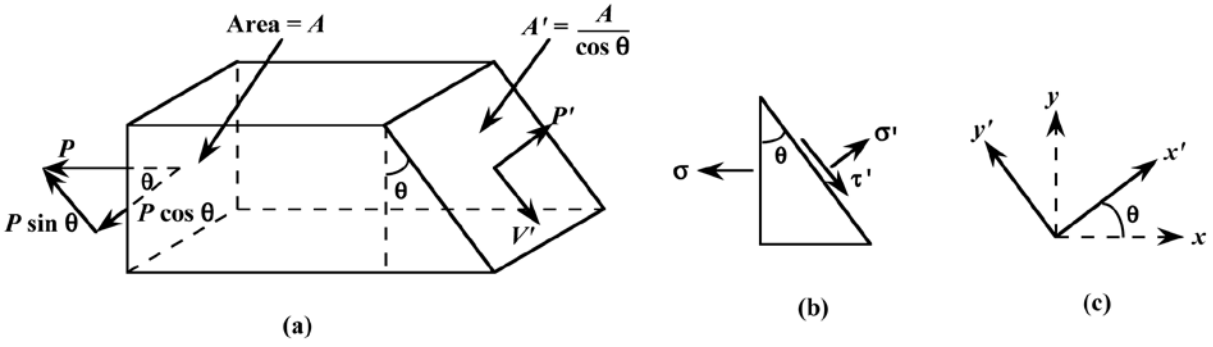
PROBLEM SOLUTIONS

Concepts of Stress and Strain

6.1 *Using mechanics of materials principles (i.e., equations of mechanical equilibrium applied to a free-body diagram), derive Equations 6.4a and 6.4b.*

Solution

This problem asks that we derive Equations 6.4a and 6.4b, using mechanics of materials principles. In Figure (a) below is shown a block element of material of cross-sectional area A that is subjected to a tensile force P. Also represented is a plane that is oriented at an angle θ referenced to the plane perpendicular to the tensile axis; the area of this plane is $A' = A/\cos\theta$. In addition, and the forces normal and parallel to this plane are labeled as P' and V', respectively. Furthermore, on the left-hand side of this block element are shown force components that are tangential and perpendicular to the inclined plane. In Figure (b) are shown the orientations of the applied stress σ, the normal stress to this plane σ', as well as the shear stress τ' taken parallel to this inclined plane. In addition, two coordinate axis systems in represented in Figure (c): the primed x and y axes are referenced to the inclined plane, whereas the unprimed x axis is taken parallel to the applied stress.



Normal and shear stresses are defined by Equations 6.1 and 6.3, respectively. However, we now chose to express these stresses in terms (i.e., general terms) of normal and shear forces (P and V) as

$$\sigma = \frac{P}{A}$$

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$$\tau = \frac{V}{A}$$

For static equilibrium in the x' direction the following condition must be met:

$$\sum F_{x'} = 0$$

which means that

$$P\tilde{O} - P\cos\theta = 0$$

Or that

$$P' = P\cos\theta$$

Now it is possible to write an expression for the stress σ' in terms of P' and A' using the above expression and the relationship between A and A' [Figure (a)]:

$$\sigma' = \frac{P\tilde{O}}{A\hat{C}}$$

$$= \frac{P\cos\theta}{\frac{A}{\cos\theta}} = \frac{P}{A}\cos^2\theta$$

However, it is the case that $P/A = \sigma$; and, after making this substitution into the above expression, we have Equation 6.4a--that is

$$\sigma' = \sigma\cos^2\theta$$

Now, for static equilibrium in the y' direction, it is necessary that

$$\sum F_{y\tilde{O}} = 0$$

$$= -V\tilde{O} + P\sin\theta$$

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Or

$$V' = P\sin\theta$$

We now write an expression for τ' as

$$\tau' = \frac{V'}{A'}$$

And, substitution of the above equation for V' and also the expression for A' gives

$$\tau' = \frac{V'}{A'}$$

$$= \frac{P\sin\theta}{\frac{A}{\cos\theta}}$$

$$= \frac{P}{A}\sin\theta\cos\theta$$

$$= \sigma\sin\theta\cos\theta$$

which is just Equation 6.4b.

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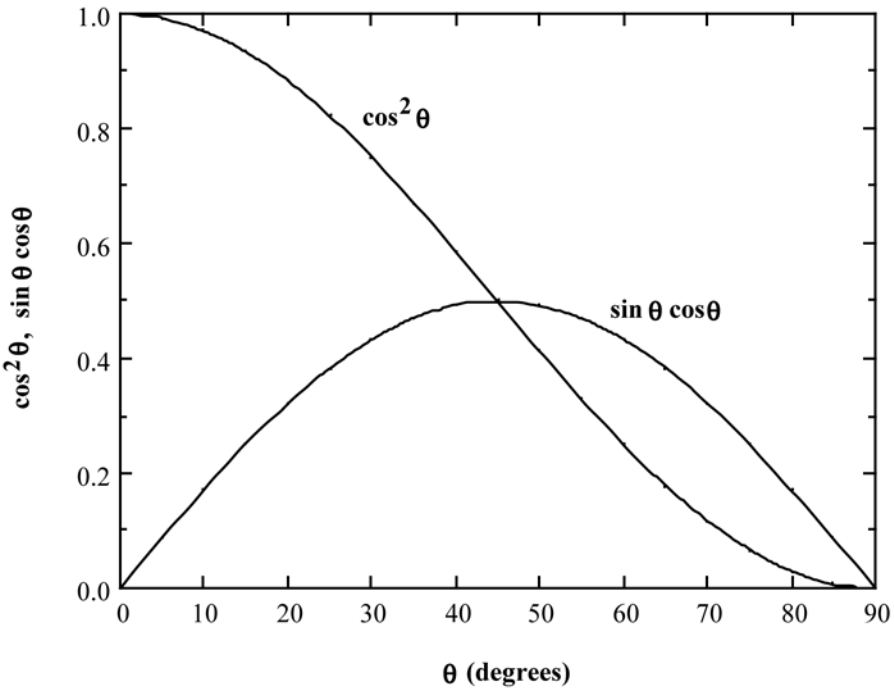
6.2 *(a) Equations 6.4a and 6.4b are expressions for normal (σ') and shear (τ') stresses, respectively, as a function of the applied tensile stress (σ) and the inclination angle of the plane on which these stresses are taken (θ of Figure 6.4). Make a plot on which is presented the orientation parameters of these expressions (i.e., $\cos^2 \theta$ and sin θ cos θ) versus θ.*

(b) From this plot, at what angle of inclination is the normal stress a maximum?

(c) Also, at what inclination angle is the shear stress a maximum?

Solution

(a) Below are plotted curves of $\cos^2\theta$ (for σ') and sin θ cos θ (for τ') versus θ.



(b) The maximum normal stress occurs at an inclination angle of 0°.

(c) The maximum shear stress occurs at an inclination angle of 45°.

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Stress-Strain Behavior

6.3 *A specimen of aluminum having a rectangular cross section 10 mm × 12.7 mm (0.4 in. × 0.5 in.) is pulled in tension with 35,500 N (8000 lb_f) force, producing only elastic deformation. Calculate the resulting strain.*

Solution

This problem calls for us to calculate the elastic strain that results for an aluminum specimen stressed in tension. The cross-sectional area is just (10 mm) × (12.7 mm) = 127 mm^2 (= 1.27×10^{-4} m^2 = 0.20 $in.^2$); also, the elastic modulus for Al is given in Table 6.1 as 69 GPa (or 69×10^9 N/m^2). Combining Equations 6.1 and 6.5 and solving for the strain yields

$$\varepsilon = \frac{\sigma}{E} = \frac{F}{A_0 E} = \frac{35{,}500 \text{ N}}{(1.27 \times 10^{-4} \text{ m}^2)(69 \times 10^9 \text{ N/m}^2)} = 4.1 \times 10^{-3}$$

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6.4 *A cylindrical specimen of a titanium alloy having an elastic modulus of 107 GPa (15.5×10^6 psi) and an original diameter of 3.8 mm (0.15 in.) will experience only elastic deformation when a tensile load of 2000 N (450 lb_f) is applied. Compute the maximum length of the specimen before deformation if the maximum allowable elongation is 0.42 mm (0.0165 in.).*

Solution

We are asked to compute the maximum length of a cylindrical titanium alloy specimen (before deformation) that is deformed elastically in tension. For a cylindrical specimen

$$A_0 = \pi\left(\frac{d_0}{2}\right)^2$$

where d_0 is the original diameter. Combining Equations 6.1, 6.2, and 6.5 and solving for l_0 leads to

$$l_0 = \frac{\Delta l}{\varepsilon} = \frac{\Delta l}{\frac{\sigma}{E}} \hat{E} \quad \frac{\Delta l\, E}{\frac{F}{A_0}} \hat{E} = \frac{\Delta l\, E\pi \left(\frac{d_0}{2}\right)^2}{F} = \frac{\Delta l\, E\pi\, d_0^2}{4F}$$

$$= \frac{(0.42 \times 10^{-3}\ \text{m})(107 \times 10^9\ \text{N/m}^2)\ (\pi)\ (3.8 \times 10^{-3}\ \text{m})^2}{(4)(2000\ \text{N})}$$

$$= 0.255\ \text{m} = 255\ \text{mm}\ (10.0\ \text{in.})$$

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6.5 *A steel bar 100 mm (4.0 in.) long and having a square cross section 20 mm (0.8 in.) on an edge is pulled in tension with a load of 89,000 N (20,000 lb_f), and experiences an elongation of 0.10 mm (4.0×10^{-3} in.). Assuming that the deformation is entirely elastic, calculate the elastic modulus of the steel.*

Solution

This problem asks us to compute the elastic modulus of steel. For a square cross-section, $A_0 = b_0^2$, where b_0 is the edge length. Combining Equations 6.1, 6.2, and 6.5 and solving for E, leads to

$$E = \frac{\sigma}{\varepsilon} = \frac{\dfrac{F}{A_0}}{\dfrac{\Delta l}{l_0}} = \frac{F l_0}{b_0^2 \Delta l}$$

$$= \frac{(89{,}000\ \text{N})(100 \times 10^{-3}\ \text{m})}{(20 \times 10^{-3}\ \text{m})^2 (0.10 \times 10^{-3}\ \text{m})}$$

$$= 223 \times 10^9\ \text{N/m}^2 = 223\ \text{GPa}\ \ (31.3 \times 10^6\ \text{psi})$$

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6.6 *Consider a cylindrical titanium wire 3.0 mm (0.12 in.) in diameter and 2.5 × 10^4 mm (1000 in.) long. Calculate its elongation when a load of 500 N (112 lb_f) is applied. Assume that the deformation is totally elastic.*

Solution

In order to compute the elongation of the Ti wire when the 500 N load is applied we must employ Equations 6.1, 6.2, and 6.5. Solving for Δl and realizing that for Ti, E = 107 GPa (15.5 × 10^6 psi) (Table 6.1),

$$\Delta l = l_0 \varepsilon = l_0 \frac{\sigma}{E} = \frac{l_0 F}{E A_0} = \frac{l_0 F}{E \pi \left(\frac{d_0}{2} \right)^2} = \frac{4 l_0 F}{E \pi d_0^2}$$

$$= \frac{(4)(25\ \text{m})(500\ \text{N})}{(107 \times 10^9\ \text{N/m}^2)(\pi)(3 \times 10^{-3}\ \text{m})^2} = 0.0165\ \text{m} = 16.5\ \text{mm}\ \ (0.65\ \text{in.})$$

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6.7 *For a bronze alloy, the stress at which plastic deformation begins is 275 MPa (40,000 psi), and the modulus of elasticity is 115 GPa (16.7×10^6 psi).*

(a) What is the maximum load that may be applied to a specimen with a cross-sectional area of 325 mm^2 ($0.5\ in.^2$) without plastic deformation?

(b) If the original specimen length is 115 mm (4.5 in.), what is the maximum length to which it may be stretched without causing plastic deformation?

Solution

(a) This portion of the problem calls for a determination of the maximum load that can be applied without plastic deformation (F_y). Taking the yield strength to be 275 MPa, and employment of Equation 6.1 leads to

$$F_y = \sigma_y A_0 = \left(275 \times 10^6\ \text{N/m}^2\right)\left(325 \times 10^{-6}\ \text{m}^2\right)$$

$$= 89{,}375\ \text{N} \quad (20{,}000\ \text{lb}_\text{f})$$

(b) The maximum length to which the sample may be deformed without plastic deformation is determined from Equations 6.2 and 6.5 as

$$l_i = l_0\left(1 + \frac{\sigma}{E}\right)$$

$$= (115\ \text{mm})\left[1 + \frac{275\ \text{MPa}}{115 \times 10^3\ \text{MPa}}\right] = 115.28\ \text{mm}\ \ (4.51\ \text{in.})$$

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6.8 *A cylindrical rod of copper (E = 110 GPa, 16 × 10^6 psi) having a yield strength of 240 MPa (35,000 psi) is to be subjected to a load of 6660 N (1500 lb_f). If the length of the rod is 380 mm (15.0 in.), what must be the diameter to allow an elongation of 0.50 mm (0.020 in.)?*

Solution

This problem asks us to compute the diameter of a cylindrical specimen of copper in order to allow an elongation of 0.50 mm. Employing Equations 6.1, 6.2, and 6.5, assuming that deformation is entirely elastic

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0^2}{4}\right)} = E\,\frac{\Delta l}{l_0}$$

Or, solving for d_0

$$d_0 = \sqrt{\frac{4\,l_0 F}{\pi\,E\,\Delta l}}$$

$$= \sqrt{\frac{(4)\left(380 \times 10^{-3}\ \text{m}\right)(6660\ \text{N})}{(\pi)\left(110 \times 10^{9}\ \text{N/m}^2\right)\left(0.50 \times 10^{-3}\ \text{m}\right)}}$$

$$= 7.65 \times 10^{-3}\ \text{m} = 7.65\ \text{mm}\ \ (0.30\ \text{in.})$$

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6.9 *Compute the elastic moduli for the following metal alloys, whose stress-strain behaviors may be observed in the "Tensile Tests" module of Virtual Materials Science and Engineering* (VMSE)*: (a) titanium, (b) tempered steel, (c) aluminum, and (d) carbon steel. How do these values compare with those presented in Table 6.1 for the same metals?*

Solution

The elastic modulus is the slope in the linear elastic region (Equation 6.10) as

$$E = \frac{\Delta\sigma}{\Delta\varepsilon} = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1}$$

Since stress-strain curves for all of the metals/alloys pass through the origin, we make take $\sigma_1 = 0$ and $\varepsilon_1 = 0$. Determinations of σ_2 and ε_2 are possible by moving the cursor to some arbitrary point in the linear region of the curve and then reading corresponding values in the "Stress" and "Strain" windows that are located below the plot.

(a) For the titanium alloy, we selected $\sigma_2 = 404.2$ MPa with its corresponding $\varepsilon_2 = 0.0038$. Therefore,

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{404.2 \text{ MPa} - 0 \text{ MPa}}{0.0038 - 0} = 106{,}400 \text{ MPa} = 106.4 \text{ GPa}$$

The elastic modulus for titanium given in Table 6.1 is 107 GPa, which is in very good agreement with this value.

(b) For the tempered steel, we selected $\sigma_2 = 962.2$ MPa with its corresponding $\varepsilon_2 = 0.0047$. Therefore,

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{962.2 \text{ MPa} - 0 \text{ MPa}}{0.0047 - 0} = 204{,}700 \text{ MPa} = 204.7 \text{ GPa}$$

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The elastic modulus for steel given in Table 6.1 is 207 GPa, which is in reasonably good agreement with this value.

(c) For the aluminum, we selected $\sigma_2 = 145.1$ MPa with its corresponding $\varepsilon_2 = 0.0021$. Therefore,

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{145.1 \text{ MPa} - 0 \text{ MPa}}{0.0021 - 0} = 69{,}100 \text{ MPa} = 69.1 \text{ GPa}$$

The elastic modulus for aluminum given in Table 6.1 is 69 GPa, which is in excellent agreement with this value.

(d) For the carbon steel, we selected $\sigma_2 = 129$ MPa with its corresponding $\varepsilon_2 = 0.0006$. Therefore,

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{129 \text{ MPa} - 0 \text{ MPa}}{0.0006 - 0} = 215{,}000 \text{ MPa} = 215 \text{ GPa}$$

The elastic modulus for steel given in Table 6.1 is 207 GPa, which is in reasonable agreement with this value.

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6.10 *Consider a cylindrical specimen of a steel alloy (Figure 6.21) 10.0 mm (0.39 in.) in diameter and 75 mm (3.0 in.) long that is pulled in tension. Determine its elongation when a load of 20,000 N (4,500 lb_f) is applied.*

Solution

This problem asks that we calculate the elongation Δl of a specimen of steel the stress-strain behavior of which is shown in Figure 6.21. First it becomes necessary to compute the stress when a load of 20,000 N is applied using Equation 6.1 as

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{20{,}000\ \text{N}}{\pi\left(\frac{10.0 \times 10^{-3}\ \text{m}}{2}\right)^2} = 255\ \text{MPa}\ \ (37{,}700\ \text{psi})$$

Referring to Figure 6.21, at this stress level we are in the elastic region on the stress-strain curve, which corresponds to a strain of 0.0012. Now, utilization of Equation 6.2 to compute the value of Δl

$$\Delta l = \varepsilon l_0 = (0.0012)(75\ \text{mm}) = 0.090\ \text{mm}\ \ (0.0036\ \text{in.})$$

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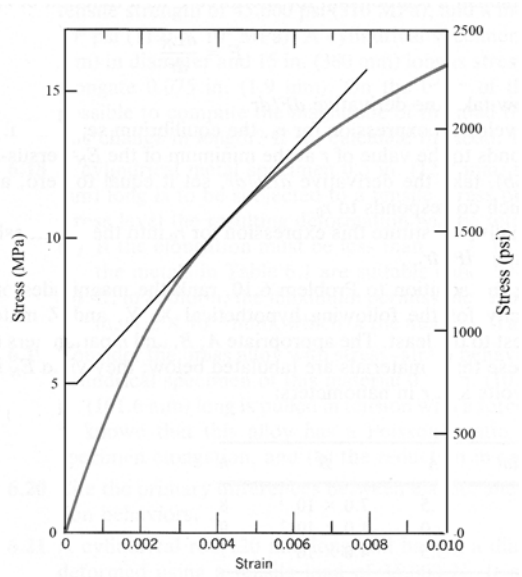
6.11 *Figure 6.22 shows, for a gray cast iron, the tensile engineering stress–strain curve in the elastic region. Determine (a) the tangent modulus at 10.3 MPa (1500 psi), and (b) the secant modulus taken to 6.9 MPa (1000 psi).*

Solution

(a) This portion of the problem asks that the tangent modulus be determined for the gray cast iron, the stress-strain behavior of which is shown in Figure 6.22. In the figure below is shown a tangent draw on the curve at a stress of 10.3 MPa (1500 psi).



The slope of this line (i.e., $\Delta\sigma/\Delta\varepsilon$), the tangent modulus, is computed as follows:

$$\frac{\Delta\sigma}{\Delta\varepsilon} = \frac{15\ \text{MPa} - 5\ \text{MPa}}{0.0074 - 0.0003} = 1410\ \text{MPa} = 1.41\ \text{GPa}\ (2.04 \times 10^5\ \text{psi})$$

(b) The secant modulus taken from the origin is calculated by taking the slope of a secant drawn from the origin through the stress-strain curve at 6.9 MPa (1,000 psi). This secant is drawn on the curve shown below:

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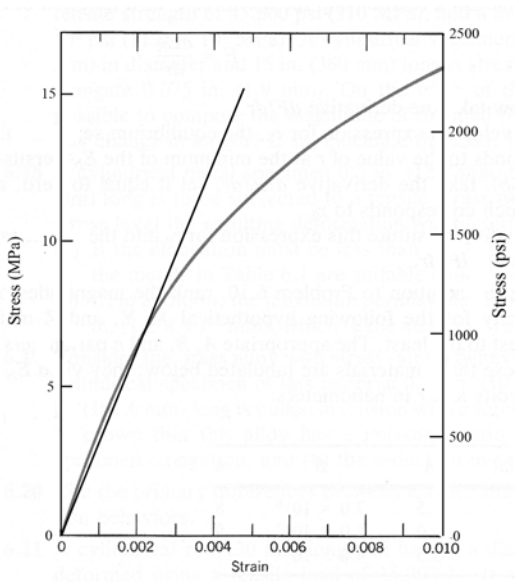

The slope of this line (i.e., $\Delta\sigma/\Delta\varepsilon$), the secant modulus, is computed as follows:

$$\frac{\Delta\sigma}{\Delta\varepsilon} = \frac{15\ \text{MPa} - 0\ \text{MPa}}{0.0047 - 0} = 3190\ \text{MPa} = 3.19\ \text{GPa}\quad (4.63 \times 10^5\ \text{psi})$$

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6.12 *As noted in Section 3.15, for single crystals of some substances, the physical properties are anisotropic; that is, they are dependent on crystallographic direction. One such property is the modulus of elasticity. For cubic single crystals, the modulus of elasticity in a general [uvw] direction, E_{uvw}, is described by the relationship*

$$\frac{1}{E_{uvw}} = \frac{1}{E_{\langle 100\rangle}} - 3\left(\frac{1}{E_{\langle 100\rangle}} - \frac{1}{E_{\langle 111\rangle}}\right)\left(\alpha^2\beta^2 + \beta^2\gamma^2 + \gamma^2\alpha^2\right)$$

where $E_{\langle 100\rangle}$ and $E_{\langle 111\rangle}$ are the moduli of elasticity in [*100*] *and* [*111*] *directions, respectively; α, β, and γ are the cosines of the angles between* [*uvw*] *and the respective* [*100*], [*010*], *and* [*001*] *directions. Verify that the $E_{\langle 110\rangle}$ values for aluminum, copper, and iron in Table 3.3 are correct.*

Solution

We are asked, using the equation given in the problem statement, to verify that the modulus of elasticity values along [110] directions given in Table 3.3 for aluminum, copper, and iron are correct. The α, β, and γ parameters in the equation correspond, respectively, to the cosines of the angles between the [110] direction and [100], [010] and [001] directions. Since these angles are 45°, 45°, and 90°, the values of α, β, and γ are 0.707, 0.707, and 0, respectively. Thus, the given equation takes the form

$$\frac{1}{E_{<110>}}$$

$$= \frac{1}{E_{<100>}} - 3\left(\frac{1}{E_{<100>}} - \frac{1}{E_{<111>}}\right)\left[(0.707)^2(0.707)^2 + (0.707)^2(0)^2 + (0)^2(0.707)^2\right]$$

$$= \frac{1}{E_{<100>}} - (0.75)\left(\frac{1}{E_{<100>}} - \frac{1}{E_{<111>}}\right)$$

Utilizing the values of $E_{<100>}$ and $E_{<111>}$ from Table 3.3 for Al

$$\frac{1}{E_{<110>}} = \frac{1}{63.7\text{ GPa}} - (0.75)\left[\frac{1}{63.7\text{ GPa}} - \frac{1}{76.1\text{ GPa}}\right]$$

Which leads to, $E_{<110>}$ = 72.6 GPa, the value cited in the table.

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For Cu,

$$\frac{1}{E_{<110>}} = \frac{1}{66.7\ \text{GPa}} - (0.75)\left[\frac{1}{66.7\ \text{GPa}} - \frac{1}{191.1\ \text{GPa}}\right]$$

Thus, $E_{<110>}$ = 130.3 GPa, which is also the value cited in the table.

Similarly, for Fe

$$\frac{1}{E_{<110>}} = \frac{1}{125.0\ \text{GPa}} - (0.75)\left[\frac{1}{125.0\ \text{GPa}} - \frac{1}{272.7\ \text{GPa}}\right]$$

And $E_{<110>}$ = 210.5 GPa, which is also the value given in the table.

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6.13 *In Section 2.6 it was noted that the net bonding energy E_N between two isolated positive and negative ions is a function of interionic distance r as follows:*

$$E_N = -\frac{A}{r} + \frac{B}{r^n} \qquad (6.25)$$

where A, B, and n are constants for the particular ion pair. Equation 6.25 is also valid for the bonding energy between adjacent ions in solid materials. The modulus of elasticity E is proportional to the slope of the interionic force–separation curve at the equilibrium interionic separation; that is,

$$E \propto \left(\frac{dF}{dr}\right)_{r_o}$$

Derive an expression for the dependence of the modulus of elasticity on these A, B, and n parameters (for the two-ion system) using the following procedure:

1. Establish a relationship for the force F as a function of r, realizing that

$$F = \frac{dE_N}{dr}$$

2. Now take the derivative dF/dr.

3. Develop an expression for r_0, the equilibrium separation. Since r_0 corresponds to the value of r at the minimum of the E_N-versus-r curve (Figure 2.8b), take the derivative dE_N/dr, set it equal to zero, and solve for r, which corresponds to r_0.

4. Finally, substitute this expression for r_0 into the relationship obtained by taking dF/dr.

Solution

This problem asks that we derive an expression for the dependence of the modulus of elasticity, *E*, on the parameters *A*, *B*, and *n* in Equation 6.25. It is first necessary to take dE_N/dr in order to obtain an expression for the force *F*; this is accomplished as follows:

$$F = \frac{dE_N}{dr} = \frac{d\left(-\frac{A}{r}\right)}{dr} + \frac{d\left(\frac{B}{r^n}\right)}{dr}$$

$$= \frac{A}{r^2} - \frac{nB}{r^{(n+1)}}$$

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The second step is to set this dE_N/dr expression equal to zero and then solve for r (= r_0). The algebra for this procedure is carried out in Problem 2.14, with the result that

$$r_0 = \left(\frac{A}{nB}\right)^{1/(1-n)}$$

Next it becomes necessary to take the derivative of the force (dF/dr), which is accomplished as follows:

$$\frac{dF}{dr} = \frac{d\left(\frac{A}{r^2}\right)}{dr} + \frac{d\left(-\frac{nB}{r^{(n+1)}}\right)}{dr}$$

$$= -\frac{2A}{r^3} + \frac{(n)(n+1)B}{r^{(n+2)}}$$

Now, substitution of the above expression for r_0 into this equation yields

$$\left(\frac{dF}{dr}\right)_{r_0} = -\frac{2A}{\left(\frac{A}{nB}\right)^{3/(1-n)}} + \frac{(n)(n+1)B}{\left(\frac{A}{nB}\right)^{(n+2)/(1-n)}}$$

which is the expression to which the modulus of elasticity is proportional.

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6.14 *Using the solution to Problem 6.13, rank the magnitudes of the moduli of elasticity for the following hypothetical X, Y, and Z materials from the greatest to the least. The appropriate A, B, and n parameters (Equation 6.25) for these three materials are tabulated below; they yield E_N in units of electron volts and r in nanometers:*

Material	***A***	***B***	***n***
X	*2.5*	2.0×10^{-5}	*8*
Y	*2.3*	8.0×10^{-6}	*10.5*
Z	*3.0*	1.5×10^{-5}	*9*

Solution

This problem asks that we rank the magnitudes of the moduli of elasticity of the three hypothetical metals X, Y, and Z. From Problem 6.13, it was shown for materials in which the bonding energy is dependent on the interatomic distance *r* according to Equation 6.25, that the modulus of elasticity *E* is proportional to

$$E \propto -\frac{2A}{\left(\frac{A}{nB}\right)^{3/(1-n)}} + \frac{(n)(n+1)B}{\left(\frac{A}{nB}\right)^{(n+2)/(1-n)}}$$

For metal X, $A = 2.5$, $B = 2.0 \times 10^{-5}$, and $n = 8$. Therefore,

$$E \propto -\frac{(2)(2.5)}{\left[\frac{2.5}{(8)\left(2 \times 10^{-5}\right)}\right]^{3/(1-8)}} + \frac{(8)(8+1)\left(2 \times 10^{-5}\right)}{\left[\frac{2.5}{(8)\left(2 \times 10^{-5}\right)}\right]^{(8+2)/(1-8)}}$$

$$= 1097$$

For metal Y, $A = 2.3$, $B = 8 \times 10^{-6}$, and $n = 10.5$. Hence

$$E \propto -\frac{(2)(2.3)}{\left[\frac{2.3}{(10.5)\left(8 \times 10^{-6}\right)}\right]^{3/(1-10.5)}} + \frac{(10.5)(10.5+1)\left(8 \times 10^{-6}\right)}{\left[\frac{2.3}{(10.5)\left(8 \times 10^{-6}\right)}\right]^{(10.5+2)/(1-10.5)}}$$

$$= 551$$

And, for metal Z, $A = 3.0$, $B = 1.5 \times 10^{-5}$, and $n = 9$. Thus

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$$E \propto -\frac{(2)(3.0)}{\left[\dfrac{3.0}{(9)\left(1.5\times10^{-5}\right)}\right]^{3/(1-9)}} + \frac{(9)(9+1)\left(1.5\times10^{-5}\right)}{\left[\dfrac{3.0}{(9)\left(1.5\times10^{-5}\right)}\right]^{(9+2)/(1-9)}}$$

$$= 1024$$

Therefore, metal X has the highest modulus of elasticity.

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Elastic Properties of Materials

6.15 *A cylindrical specimen of aluminum having a diameter of 19 mm (0.75 in.) and length of 200 mm (8.0 in.) is deformed elastically in tension with a force of 48,800 N (11,000 lb_f). Using the data contained in Table 6.1, determine the following:*

(a) The amount by which this specimen will elongate in the direction of the applied stress.

(b) The change in diameter of the specimen. Will the diameter increase or decrease?

Solution

(a) We are asked, in this portion of the problem, to determine the elongation of a cylindrical specimen of aluminum. Combining Equations 6.1, 6.2, and 6.5, leads to

$$\sigma = E\varepsilon$$

$$\frac{F}{\pi\left(\frac{d_0^2}{4}\right)} = E\,\frac{\Delta l}{l_0}$$

Or, solving for Δl (and realizing that E = 69 GPa, Table 6.1), yields

$$\Delta l = \frac{4F\,l_0}{\pi\,d_0^2 E}$$

$$= \frac{(4)(48{,}800\ \text{N})\left(200 \times 10^{-3}\ \text{m}\right)}{(\pi)\left(19 \times 10^{-3}\ \text{m}\right)^2\left(69 \times 10^{9}\ \text{N/m}^2\right)} = 5 \times 10^{-4}\ \text{m} = 0.50\ \text{mm}\ \ (0.02\ \text{in.})$$

(b) We are now called upon to determine the change in diameter, Δd. Using Equation 6.8

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\Delta d / d_0}{\Delta l / l_0}$$

From Table 6.1, for aluminum, ν = 0.33. Now, solving the above expression for Δd yields

$$\Delta d = -\frac{\nu\,\Delta l\,d_0}{l_0} = -\frac{(0.33)(0.50\ \text{mm})(19\ \text{mm})}{200\ \text{mm}}$$

$$= -1.6 \times 10^{-2}\ \text{mm}\ \ (-6.2 \times 10^{-4}\ \text{in.})$$

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The diameter will decrease.

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6.16 *A cylindrical bar of steel 10 mm (0.4 in.) in diameter is to be deformed elastically by application of a force along the bar axis. Using the data in Table 6.1, determine the force that will produce an elastic reduction of 3 $\times 10^{-3}$ mm (1.2×10^{-4} in.) in the diameter.*

Solution

This problem asks that we calculate the force necessary to produce a reduction in diameter of 3×10^{-3} mm for a cylindrical bar of steel. For a cylindrical specimen, the cross-sectional area is equal to

$$A_0 = \frac{\pi d_0^2}{4}$$

Now, combining Equations 6.1 and 6.5 leads to

$$\sigma = \frac{F}{A_0} = \frac{F}{\frac{\pi d_0^2}{4}} = E\varepsilon_z$$

And, since from Equation 6.8

$$\varepsilon_z = -\frac{\varepsilon_x}{\nu} = -\frac{\frac{\Delta d}{d_0}}{\nu} = -\frac{\Delta d}{\nu d_0}$$

Substitution of this equation into the above expression gives

$$\frac{F}{\frac{\pi d_0^2}{4}} = E\left(-\frac{\Delta d}{\nu d_0}\right)$$

And, solving for F leads to

$$F = -\frac{d_0 \Delta d\, \pi E}{4\nu}$$

From Table 6.1, for steel, $\nu = 0.30$ and $E = 207$ GPa. Thus,

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$$F = -\frac{(10 \times 10^{-3}\ \text{m})(-3.0 \times 10^{-6}\ \text{m})(\pi)(207 \times 10^{9}\ \text{N/m}^2)}{(4)(0.30)}$$

$$= 16{,}250\ \text{N}\ \ (3770\ \text{lb}_\text{f})$$

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6.17 *A cylindrical specimen of some alloy 8 mm (0.31 in.) in diameter is stressed elastically in tension. A force of 15,700 N (3530 lb_f) produces a reduction in specimen diameter of 5 × 10^{-3} mm (2 × 10^{-4} in.). Compute Poisson's ratio for this material if its modulus of elasticity is 140 GPa (20.3 × 10^6 psi).*

Solution

This problem asks that we compute Poisson's ratio for the metal alloy. From Equations 6.5 and 6.1

$$\varepsilon_z = \frac{\sigma}{E} = \frac{F}{A_0 E} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2 E} = \frac{4F}{\pi d_0^2 E}$$

Since the transverse strain ε_x is just

$$\varepsilon_x = \frac{\Delta d}{d_0}$$

and Poisson's ratio is defined by Equation 6.8, then

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\Delta d / d_0}{\left(\frac{4F}{\pi d_0^2 E}\right)} = -\frac{d_0 \Delta d\, \pi E}{4F}$$

$$= -\frac{(8 \times 10^{-3}\ \text{m})(-5 \times 10^{-6}\ \text{m})\ (\pi)(140 \times 10^9\ \text{N/m}^2)}{(4)(15{,}700\ \text{N})} = 0.280$$

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6.18 *A cylindrical specimen of a hypothetical metal alloy is stressed in compression. If its original and final diameters are 20.000 and 20.025 mm, respectively, and its final length is 74.96 mm, compute its original length if the deformation is totally elastic. The elastic and shear moduli for this alloy are 105 GPa and 39.7 GPa, respectively.*

Solution

This problem asks that we compute the original length of a cylindrical specimen that is stressed in compression. It is first convenient to compute the lateral strain ε_x as

$$\varepsilon_x = \frac{\Delta d}{d_0} = \frac{20.025\ \text{mm} - 20.000\ \text{mm}}{20.000\ \text{mm}} = 1.25 \times 10^{-3}$$

In order to determine the longitudinal strain ε_z we need Poisson's ratio, which may be computed using Equation 6.9; solving for ν yields

$$\nu = \frac{E}{2G} - 1 = \frac{105 \times 10^3\ \text{MPa}}{(2)(39.7 \times 10^3\ \text{MPa})} - 1 = 0.322$$

Now ε_z may be computed from Equation 6.8 as

$$\varepsilon_z = -\frac{\varepsilon_x}{\nu} = -\frac{1.25 \times 10^{-3}}{0.322} = -3.88 \times 10^{-3}$$

Now solving for l_0 using Equation 6.2

$$l_0 = \frac{l_i}{1 + \varepsilon_z}$$

$$= \frac{74.96\ \text{mm}}{1 - 3.88 \times 10^{-3}} = 75.25\ \text{mm}$$

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6.19 *Consider a cylindrical specimen of some hypothetical metal alloy that has a diameter of 8.0 mm (0.31 in.). A tensile force of 1000 N (225 lb_f) produces an elastic reduction in diameter of 2.8×10^{-4} mm (1.10×10^{-5} in.). Compute the modulus of elasticity for this alloy, given that Poisson's ratio is 0.30.*

Solution

This problem asks that we calculate the modulus of elasticity of a metal that is stressed in tension. Combining Equations 6.5 and 6.1 leads to

$$E = \frac{\sigma}{\varepsilon_z} = \frac{F}{A_0 \varepsilon_z} = \frac{F}{\varepsilon_z \pi \left(\frac{d_0}{2}\right)^2} = \frac{4F}{\varepsilon_z \pi d_0^2}$$

From the definition of Poisson's ratio, (Equation 6.8) and realizing that for the transverse strain, $\varepsilon_x = \frac{\Delta d}{d_0}$

$$\varepsilon_z = -\frac{\varepsilon_x}{\nu} = -\frac{\Delta d}{d_0 \nu}$$

Therefore, substitution of this expression for ε_z into the above equation yields

$$E = \frac{4F}{\varepsilon_z \pi d_0^2} = \frac{4F\nu}{\pi d_0 \Delta d}$$

$$= \frac{(4)(1000\ \text{N})(0.30)}{\pi\left(8 \times 10^{-3}\ \text{m}\right)\left(2.8 \times 10^{-7}\ \text{m}\right)} = 1.705 \times 10^{11}\ \text{Pa} = 170.5\ \text{GPa}\ \ (24.7 \times 10^6\ \text{psi})$$

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6.20 *A brass alloy is known to have a yield strength of 275 MPa (40,000 psi), a tensile strength of 380 MPa (55,000 psi), and an elastic modulus of 103 GPa (15.0×10^6 psi). A cylindrical specimen of this alloy 12.7 mm (0.50 in.) in diameter and 250 mm (10.0 in.) long is stressed in tension and found to elongate 7.6 mm (0.30 in.). On the basis of the information given, is it possible to compute the magnitude of the load that is necessary to produce this change in length? If so, calculate the load. If not, explain why.*

Solution

We are asked to ascertain whether or not it is possible to compute, for brass, the magnitude of the load necessary to produce an elongation of 7.6 mm (0.30 in.). It is first necessary to compute the strain at yielding from the yield strength and the elastic modulus, and then the strain experienced by the test specimen. Then, if

$$\varepsilon(\text{test}) < \varepsilon(\text{yield})$$

deformation is elastic, and the load may be computed using Equations 6.1 and 6.5. However, if

$$\varepsilon(\text{test}) > \varepsilon(\text{yield})$$

computation of the load is not possible inasmuch as deformation is plastic and we have neither a stress-strain plot nor a mathematical expression relating plastic stress and strain. We compute these two strain values as

$$\varepsilon(\text{test}) = \frac{\Delta l}{l_0} = \frac{7.6 \text{ mm}}{250 \text{ mm}} = 0.03$$

and

$$\varepsilon(\text{yield}) = \frac{\sigma_y}{E} = \frac{275 \text{ MPa}}{103 \times 10^3 \text{ MPa}} = 0.0027$$

Therefore, computation of the load is *not possible* since $\varepsilon(\text{test}) > \varepsilon(\text{yield})$.

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6.21 *A cylindrical metal specimen 12.7 mm (0.5 in.) in diameter and 250 mm (10 in.) long is to be subjected to a tensile stress of 28 MPa (4000 psi); at this stress level the resulting deformation will be totally elastic.*

(a) If the elongation must be less than 0.080 mm (3.2×10^{-3} in.), which of the metals in Table 6.1 are suitable candidates? Why?

(b) If, in addition, the maximum permissible diameter decrease is 1.2×10^{-3} mm (4.7×10^{-5} in.) when the tensile stress of 28 MPa is applied, which of the metals that satisfy the criterion in part (a) are suitable candidates? Why?

Solution

(a) This part of the problem asks that we ascertain which of the metals in Table 6.1 experience an elongation of less than 0.080 mm when subjected to a tensile stress of 28 MPa. The maximum strain that may be sustained, (using Equation 6.2) is just

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{0.080 \text{ mm}}{250 \text{ mm}} = 3.2 \times 10^{-4}$$

Since the stress level is given (50 MPa), using Equation 6.5 it is possible to compute the minimum modulus of elasticity which is required to yield this minimum strain. Hence

$$E = \frac{\sigma}{\varepsilon} = \frac{28 \text{ MPa}}{3.2 \times 10^{-4}} = 87.5 \text{ GPa}$$

Which means that those metals with moduli of elasticity greater than this value are acceptable candidates—namely, brass, Cu, Ni, steel, Ti and W.

(b) This portion of the problem further stipulates that the maximum permissible diameter decrease is 1.2×10^{-3} mm when the tensile stress of 28 MPa is applied. This translates into a maximum lateral strain $\varepsilon_x(\text{max})$ as

$$\varepsilon_x(\text{max}) = \frac{\Delta d}{d_0} = \frac{-1.2 \times 10^{-3} \text{ mm}}{12.7 \text{ mm}} = -9.45 \times 10^{-5}$$

But, since the specimen contracts in this lateral direction, and we are concerned that this strain be less than 9.45×10^{-5}, then the criterion for this part of the problem may be stipulated as $-\frac{\Delta d}{d_0} < 9.45 \times 10^{-5}$.

Now, Poisson's ratio is defined by Equation 6.8 as

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$$\nu = -\frac{\varepsilon_x}{\varepsilon_z}$$

For each of the metal alloys let us consider a possible lateral strain, $\varepsilon_x = \frac{\Delta d}{d_0}$. Furthermore, since the deformation is elastic, then, from Equation 6.5, the longitudinal strain, ε_z is equal to

$$\varepsilon_z = \frac{\sigma}{E}$$

Substituting these expressions for ε_x and ε_z into the definition of Poisson's ratio we have

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\frac{\Delta d}{d_0}}{\frac{\sigma}{E}}$$

which leads to the following:

$$-\frac{\Delta d}{d_0} = \frac{\nu \sigma}{E}$$

Using values for ν and E found in Table 6.1 for the six metal alloys that satisfy the criterion for part (a), and for σ = 28 MPa, we are able to compute a $-\frac{\Delta d}{d_0}$ for each alloy as follows:

$$-\frac{\Delta d}{d_0}(\text{brass}) = \frac{(0.34)(28 \times 10^6\ \text{N/m}^2)}{97 \times 10^9\ \text{N/m}^2} = 9.81 \times 10^{-5}$$

$$-\frac{\Delta d}{d_0}(\text{copper}) = \frac{(0.34)(28 \times 10^6\ \text{N/m}^2)}{110 \times 10^9\ \text{N/m}^2} = 8.65 \times 10^{-5}$$

$$-\frac{\Delta d}{d_0}(\text{titanium}) = \frac{(0.34)(28 \times 10^6\ \text{N/m}^2)}{107 \times 10^9\ \text{N/m}^2} = 8.90 \times 10^{-5}$$

$$-\frac{\Delta d}{d_0}(\text{nickel}) = \frac{(0.31)(28 \times 10^6\ \text{N/m}^2)}{207 \times 10^9\ \text{N/m}^2} = 4.19 \times 10^{-5}$$

$$-\frac{\Delta d}{d_0}(\text{steel}) = \frac{(0.30)(28 \times 10^6\ \text{N/m}^2)}{207 \times 10^9\ \text{N/m}^2} = 4.06 \times 10^{-5}$$

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$$-\frac{\Delta d}{d_0}(\text{tungsten}) = \frac{(0.28)(28 \times 10^6\ \text{N/m}^2)}{407 \times 10^9\ \text{N/m}^2} = 1.93 \times 10^{-5}$$

Thus, of the above six alloys, only brass will have a negative transverse strain that is greater than 9.45×10^{-5}. This means that the following alloys satisfy the criteria for both parts (a) and (b) of the problem: copper, titanium, nickel, steel, and tungsten.

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6.22 *Consider the brass alloy for which the stress-strain behavior is shown in Figure 6.12. A cylindrical specimen of this material 6 mm (0.24 in.) in diameter and 50 mm (2 in.) long is pulled in tension with a force of 5000 N (1125 lb_f). If it is known that this alloy has a Poisson's ratio of 0.30, compute: (a) the specimen elongation, and (b) the reduction in specimen diameter.*

Solution

(a) This portion of the problem asks that we compute the elongation of the brass specimen. The first calculation necessary is that of the applied stress using Equation 6.1, as

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{5000\ \text{N}}{\pi\left(\frac{6 \times 10^{-3}\ \text{m}}{2}\right)^2} = 177 \times 10^6\ \text{N/m}^2 = 177\ \text{MPa}\ \ (25{,}000\ \text{psi})$$

From the stress-strain plot in Figure 6.12, this stress corresponds to a strain of about 2.0×10^{-3}. From the definition of strain, Equation 6.2

$$\Delta l = \varepsilon l_0 = \left(2.0 \times 10^{-3}\right)(50\ \text{mm}) = 0.10\ \text{mm}\quad (4 \times 10^{-3}\ \text{in.})$$

(b) In order to determine the reduction in diameter Δd, it is necessary to use Equation 6.8 and the definition of lateral strain (i.e., $\varepsilon_x = \Delta d/d_0$) as follows

$$\Delta d = d_0\varepsilon_x = -d_0\nu\varepsilon_z = -(6\ \text{mm})(0.30)\left(2.0 \times 10^{-3}\right)$$

$$= -3.6 \times 10^{-3}\ \text{mm}\ \ (-1.4 \times 10^{-4}\ \text{in.})$$

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6.23 *A cylindrical rod 100 mm long and having a diameter of 10.0 mm is to be deformed using a tensile load of 27,500 N. It must not experience either plastic deformation or a diameter reduction of more than 7.5 × 10^{-3} mm. Of the materials listed as follows, which are possible candidates? Justify your choice(s).*

Material	***Modulus of Elasticity (GPa)***	***Yield Strength (MPa)***	***Poisson's Ratio***
Aluminum alloy	*70*	*200*	*0.33*
Brass alloy	*101*	*300*	*0.34*
Steel alloy	*207*	*400*	*0.30*
Titanium alloy	*107*	*650*	*0.34*

Solution

This problem asks that we assess the four alloys relative to the two criteria presented. The first criterion is that the material not experience plastic deformation when the tensile load of 27,500 N is applied; this means that the stress corresponding to this load not exceed the yield strength of the material. Upon computing the stress

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{27{,}500\ \text{N}}{\pi\left(\frac{10 \times 10^{-3}\ \text{m}}{2}\right)^2} = 350 \times 10^6\ \text{N/m}^2 = 350\ \text{MPa}$$

Of the alloys listed, the Ti and steel alloys have yield strengths greater than 350 MPa.

Relative to the second criterion (i.e., that Δd be less than 7.5 × 10^{-3} mm), it is necessary to calculate the change in diameter Δd for these three alloys. From Equation 6.8

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\frac{\Delta d}{d_0}}{\frac{\sigma}{E}} = -\frac{E\,\Delta d}{\sigma\, d_0}$$

Now, solving for Δd from this expression,

$$\Delta d = -\frac{\nu\,\sigma\, d_0}{E}$$

For the steel alloy

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$$\Delta d = -\frac{(0.30)(350\ \text{MPa})(10\ \text{mm})}{207 \times 10^3\ \text{MPa}} = -5.1 \times 10^{-3}\ \text{mm}$$

Therefore, the steel is a candidate.

For the Ti alloy

$$\Delta d = -\frac{(0.34)(350\ \text{MPa})(10\ \text{mm})}{107 \times 10^3\ \text{MPa}} = -11.1 \times 10^{-3}\ \text{mm}$$

Hence, the titanium alloy is *not* a candidate.

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6.24 *A cylindrical rod 380 mm (15.0 in.) long, having a diameter of 10.0 mm (0.40 in.), is to be subjected to a tensile load. If the rod is to experience neither plastic deformation nor an elongation of more than 0.9 mm (0.035 in.) when the applied load is 24,500 N (5500 lb_f), which of the four metals or alloys listed below are possible candidates? Justify your choice(s).*

Material	***Modulus of Elasticity (GPa)***	***Yield Strength (MPa)***	***Tensile Strength (MPa)***
Aluminum alloy	*70*	*255*	*420*
Brass alloy	*100*	*345*	*420*
Copper	*110*	*250*	*290*
Steel alloy	*207*	*450*	*550*

Solution

This problem asks that we ascertain which of four metal alloys will not (1) experience plastic deformation, and (2) elongate more than 0.9 mm when a tensile load of 24,500 N is applied. It is first necessary to compute the stress using Equation 6.1; a material to be used for this application must necessarily have a yield strength greater than this value. Thus,

$$\sigma = \frac{F}{A_0} = \frac{24,500\ \text{N}}{\pi\left(\frac{10.0 \times 10^{-3}\ \text{m}}{2}\right)^2} = 312\ \text{MPa}$$

Of the metal alloys listed, only brass and steel have yield strengths greater than this stress.

Next, we must compute the elongation produced in both brass and steel using Equations 6.2 and 6.5 in order to determine whether or not this elongation is less than 0.9 mm. For brass

$$\Delta l = \frac{\sigma l_0}{E} = \frac{(312\ \text{MPa})(380\ \text{mm})}{100 \times 10^3\ \text{MPa}} = 1.19\ \text{mm}$$

Thus, brass is not a candidate. However, for steel

$$\Delta l = \frac{\sigma l_0}{E} = \frac{(312\ \text{MPa})(380\ \text{mm})}{207 \times 10^3\ \text{MPa}} = 0.57\ \text{mm}$$

Therefore, of these four alloys, only steel satisfies the stipulated criteria.

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Tensile Properties

6.25 *Figure 6.21 shows the tensile engineering stress–strain behavior for a steel alloy.*

(a) What is the modulus of elasticity?

(b) What is the proportional limit?

(c) What is the yield strength at a strain offset of 0.002?

(d) What is the tensile strength?

Solution

Using the stress-strain plot for a steel alloy (Figure 6.21), we are asked to determine several of its mechanical characteristics.

(a) The elastic modulus is just the slope of the initial linear portion of the curve; or, from the inset and using Equation 6.10

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{(200 - 0)\ \text{MPa}}{(0.0010 - 0)} = 200 \times 10^3\ \text{MPa} = 200\ \text{GPa}\ \ (29 \times 10^6\ \text{psi})$$

The value given in Table 6.1 is 207 GPa.

(b) The proportional limit is the stress level at which linearity of the stress-strain curve ends, which is approximately 300 MPa (43,500 psi).

(c) The 0.002 strain offset line intersects the stress-strain curve at approximately 400 MPa (58,000 psi).

(d) The tensile strength (the maximum on the curve) is approximately 515 MPa (74,700 psi).

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6.26 *A cylindrical specimen of a brass alloy having a length of 60 mm (2.36 in.) must elongate only 10.8 mm (0.425 in.) when a tensile load of 50,000 N (11,240 lb_f) is applied. Under these circumstances, what must be the radius of the specimen? Consider this brass alloy to have the stress-strain behavior shown in Figure 6.12.*

Solution

We are asked to calculate the radius of a cylindrical brass specimen in order to produce an elongation of 10.8 mm when a load of 50,000 N is applied. It first becomes necessary to compute the strain corresponding to this elongation using Equation 6.2 as

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{10.8 \text{ mm}}{60 \text{ mm}} = 0.18$$

From Figure 6.12, a stress of 420 MPa (61,000 psi) corresponds to this strain. Since for a cylindrical specimen, stress, force, and initial radius r_0 are related as

$$\sigma = \frac{F}{\pi r_0^2}$$

then

$$r_0 = \sqrt{\frac{F}{\pi \sigma}} = \sqrt{\frac{50{,}000 \text{ N}}{\pi \left(420 \times 10^6 \text{ N/m}^2\right)}} = 0.0062 \text{ m} = 6.2 \text{ mm} \quad (0.24 \text{ in.})$$

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6.27 *A load of 85,000 N (19,100 lb_f) is applied to a cylindrical specimen of a steel alloy (displaying the stress–strain behavior shown in Figure 6.21) that has a cross-sectional diameter of 15 mm (0.59 in.).*

(a) Will the specimen experience elastic and/or plastic deformation? Why?

(b) If the original specimen length is 250 mm (10 in.), how much will it increase in length when this load is applied?

Solution

This problem asks us to determine the deformation characteristics of a steel specimen, the stress-strain behavior for which is shown in Figure 6.21.

(a) In order to ascertain whether the deformation is elastic or plastic, we must first compute the stress, then locate it on the stress-strain curve, and, finally, note whether this point is on the elastic or plastic region. Thus, from Equation 6.1

$$\sigma = \frac{F}{A_0} = \frac{85{,}000\ \text{N}}{\pi\left(\frac{15 \times 10^{-3}\ \text{m}}{2}\right)^2} = 481 \times 10^6\ \text{N/m}^2 = 481\ \text{MPa}\ \ (69{,}900\ \text{psi})$$

The 481 MPa point is beyond the linear portion of the curve, and, therefore, the deformation will be both elastic and plastic.

(b) This portion of the problem asks us to compute the increase in specimen length. From the stress-strain curve, the strain at 481 MPa is approximately 0.0135. Thus, from Equation 6.2

$$\Delta l = \varepsilon l_0 = (0.0135)(250\ \text{mm}) = 3.4\ \text{mm}\ \ (0.135\ \text{in.})$$

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6.28 *A bar of a steel alloy that exhibits the stress-strain behavior shown in Figure 6.21 is subjected to a tensile load; the specimen is 300 mm (12 in.) long, and of square cross section 4.5 mm (0.175 in.) on a side.*

(a) Compute the magnitude of the load necessary to produce an elongation of 0.45 mm (0.018 in.).

(b) What will be the deformation after the load has been released?

Solution

(a) We are asked to compute the magnitude of the load necessary to produce an elongation of 0.45 mm for the steel displaying the stress-strain behavior shown in Figure 6.21. First, calculate the strain, and then the corresponding stress from the plot.

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{0.45 \text{ mm}}{300 \text{ mm}} = 1.5 \times 10^{-3}$$

This is near the end of the elastic region; from the inset of Figure 6.21, this corresponds to a stress of about 300 MPa (43,500 psi). Now, from Equation 6.1

$$F = \sigma A_0 = \sigma b^2$$

in which b is the cross-section side length. Thus,

$$F = \left(300 \times 10^6 \text{ N/m}^2\right)\left(4.5 \times 10^{-3} \text{ m}\right)^2 = 6075 \text{ N} \quad (1366 \text{ lb}_\text{f})$$

(b) After the load is released there will be no deformation since the material was strained only elastically.

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6.29 *A cylindrical specimen of aluminum having a diameter of 0.505 in. (12.8 mm) and a gauge length of 2.000 in. (50.800 mm) is pulled in tension. Use the load–elongation characteristics tabulated below to complete parts (a) through (f).*

Load		***Length***	
N	***lb_f***	***mm***	***in.***
0	*0*	*50.800*	*2.000*
7,330	*1,650*	*50.851*	*2.002*
15,100	*3,400*	*50.902*	*2.004*
23,100	*5,200*	*50.952*	*2.006*
30,400	*6,850*	*51.003*	*2.008*
34,400	*7,750*	*51.054*	*2.010*
38,400	*8,650*	*51.308*	*2.020*
41,300	*9,300*	*51.816*	*2.040*
44,800	*10,100*	*52.832*	*2.080*
46,200	*10,400*	*53.848*	*2.120*
47,300	*10,650*	*54.864*	*2.160*
47,500	*10,700*	*55.880*	*2.200*
46,100	*10,400*	*56.896*	*2.240*
44,800	*10,100*	*57.658*	*2.270*
42,600	*9,600*	*58.420*	*2.300*
36,400	*8,200*	*59.182*	*2.330*
Fracture			

(a) Plot the data as engineering stress versus engineering strain.

(b) Compute the modulus of elasticity.

(c) Determine the yield strength at a strain offset of 0.002.

(d) Determine the tensile strength of this alloy.

(e) What is the approximate ductility, in percent elongation?

(f) Compute the modulus of resilience.

Solution

This problem calls for us to make a stress-strain plot for aluminum, given its tensile load-length data, and then to determine some of its mechanical characteristics.

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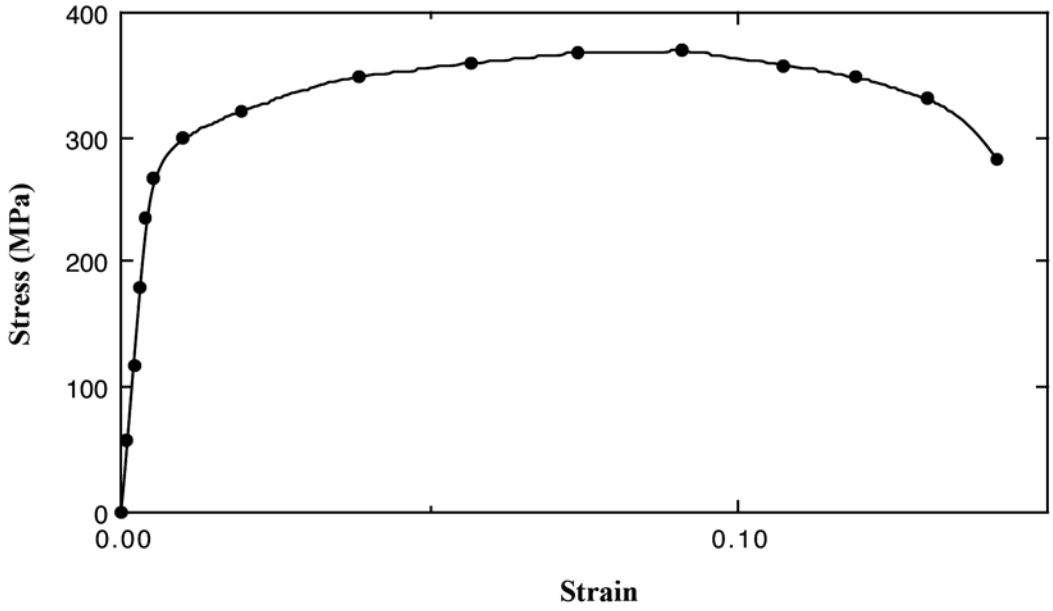
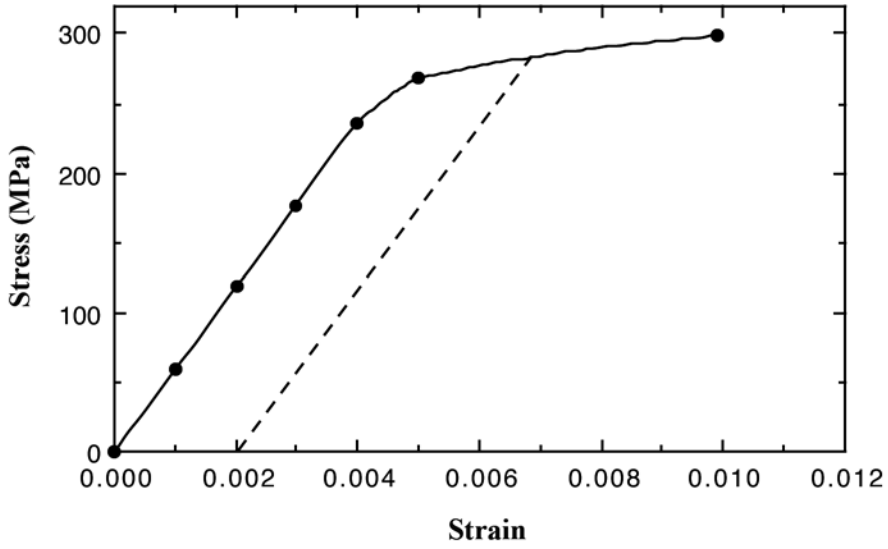
(a) The data are plotted below on two plots: the first corresponds to the entire stress-strain curve, while for the second, the curve extends to just beyond the elastic region of deformation.





(b) The elastic modulus is the slope in the linear elastic region (Equation 6.10) as

$$E = \frac{\Delta\sigma}{\Delta\varepsilon} = \frac{200\ \text{MPa} - 0\ \text{MPa}}{0.0032 - 0} = 62.5 \times 10^3\ \text{MPa} = 62.5\ \text{GPa} \quad (9.1 \times 10^6\ \text{psi})$$

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(c) For the yield strength, the 0.002 strain offset line is drawn dashed. It intersects the stress-strain curve at approximately 285 MPa (41,000 psi).

(d) The tensile strength is approximately 370 MPa (54,000 psi), corresponding to the maximum stress on the complete stress-strain plot.

(e) The ductility, in percent elongation, is just the plastic strain at fracture, multiplied by one-hundred. The total fracture strain at fracture is 0.165; subtracting out the elastic strain (which is about 0.005) leaves a plastic strain of 0.160. Thus, the ductility is about 16%EL.

(f) From Equation 6.14, the modulus of resilience is just

$$U_r = \frac{\sigma_y^2}{2E}$$

which, using data computed above gives a value of

$$U_r = \frac{(285\ \text{MPa})^2}{(2)(62.5 \times 10^3\ \text{MPa})} = 0.65\ \text{MN/m}^2 = 0.65 \times 10^6\ \text{N/m}^2 = 6.5 \times 10^5\ \text{J/m}^3 \quad (93.8\ \text{in.-lb}_f/\text{in.}^3)$$

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6.30 *A specimen of ductile cast iron having a rectangular cross section of dimensions 4.8 mm × 15.9 mm (3/16 in. × 5/8 in.) is deformed in tension. Using the load-elongation data tabulated below, complete problems (a) through (f).*

Load		***Length***	
N	***lb_f***	***mm***	***in.***
0	*0*	*75.000*	*2.953*
4,740	*1,065*	*75.025*	*2.954*
9,140	*2,055*	*75.050*	*2.955*
12,920	*2,900*	*75.075*	*2.956*
16,540	*3,720*	*75.113*	*2.957*
18,300	*4,110*	*75.150*	*2.959*
20,170	*4,530*	*75.225*	*2.962*
22,900	*5,145*	*75.375*	*2.968*
25,070	*5,635*	*75.525*	*2.973*
26,800	*6,025*	*75.750*	*2.982*
28,640	*6,440*	*76.500*	*3.012*
30,240	*6,800*	*78.000*	*3.071*
31,100	*7,000*	*79.500*	*3.130*
31,280	*7,030*	*81.000*	*3.189*
30,820	*6,930*	*82.500*	*3.248*
29,180	*6,560*	*84.000*	*3.307*
27,190	*6,110*	*85.500*	*3.366*
24,140	*5,430*	*87.000*	*3.425*
18,970	*4,265*	*88.725*	*3.493*
		Fracture	

(a) Plot the data as engineering stress versus engineering strain.

(b) Compute the modulus of elasticity.

(c) Determine the yield strength at a strain offset of 0.002.

(d) Determine the tensile strength of this alloy.

(e) Compute the modulus of resilience.

(f) What is the ductility, in percent elongation?

Solution

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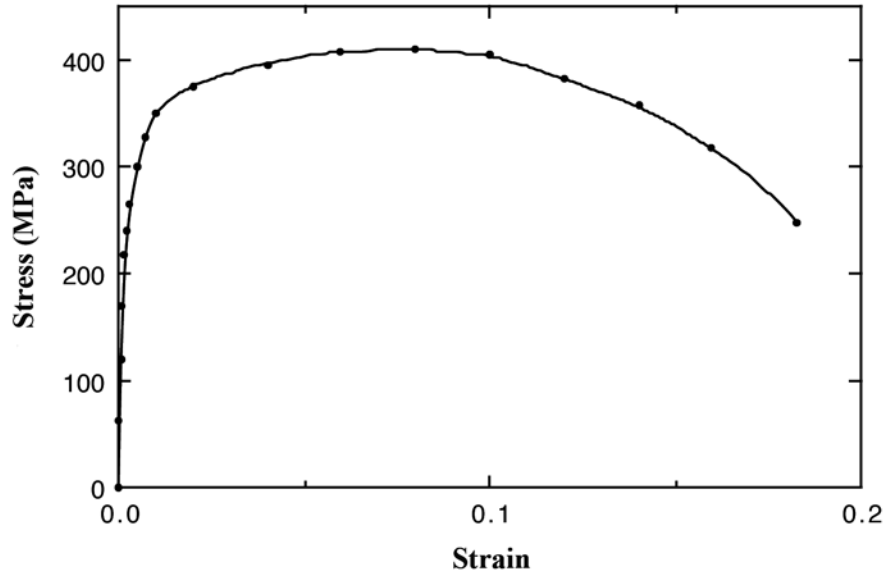
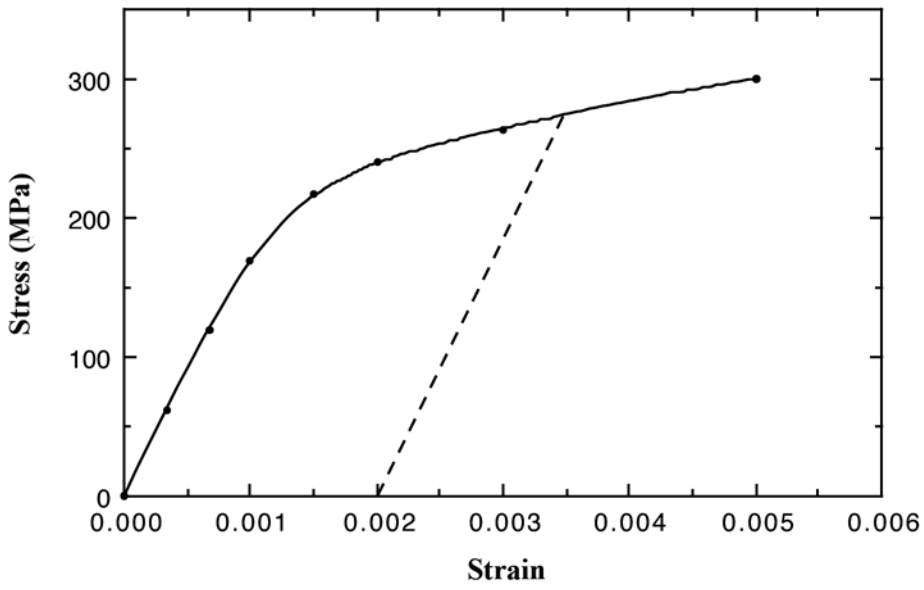
This problem calls for us to make a stress-strain plot for a ductile cast iron, given its tensile load-length data, and then to determine some of its mechanical characteristics.

(a) The data are plotted below on two plots: the first corresponds to the entire stress-strain curve, while for the second, the curve extends just beyond the elastic region of deformation.





(b) The elastic modulus is the slope in the linear elastic region (Equation 6.10) as

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$$E = \frac{\Delta\sigma}{\Delta\varepsilon} = \frac{100\ \text{MPa} - 0\ \text{MPa}}{0.0005 - 0} = 200 \times 10^3\ \text{MPa} = 200\ \text{GPa} \quad (29 \times 10^6\ \text{psi})$$

(c) For the yield strength, the 0.002 strain offset line is drawn dashed. It intersects the stress-strain curve at approximately 280 MPa (40,500 psi).

(d) The tensile strength is approximately 410 MPa (59,500 psi), corresponding to the maximum stress on the complete stress-strain plot.

(e) From Equation 6.14, the modulus of resilience is just

$$U_r = \frac{\sigma_y^2}{2E}$$

which, using data computed above, yields a value of

$$U_r = \frac{(280 \times 10^6\ \text{N/m}^2)^2}{(2)(200 \times 10^9\ \text{N/m}^2)} = 1.96 \times 10^5\ \text{J/m}^3 \quad (28.3\ \text{in.-lb}_\text{f}/\text{in.}^3)$$

(f) The ductility, in percent elongation, is just the plastic strain at fracture, multiplied by one-hundred. The total fracture strain at fracture is 0.185; subtracting out the elastic strain (which is about 0.001) leaves a plastic strain of 0.184. Thus, the ductility is about 18.4%EL.

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6.31 *For the titanium alloy, whose stress strain behavior may be observed in the "Tensile Tests" module of Virtual Materials Science and Engineering (VMSE), determine the following:*

(a) the approximate yield strength (0.002 strain offset),

(b) the tensile strength, and

(c) the approximate ductility, in percent elongation.

How do these values compare with those for the two Ti-6Al-4V alloys presented in Table B.4 of Appendix B?

Solution

(a) It is possible to do a screen capture and then print out the entire stress-strain curve for the Ti alloy. The intersection of a straight line parallel to the initial linear region of the curve and offset at a strain of 0.002 with this curve is at approximately 720 MPa.

(b) The maximum reading in the stress window located below the plot as the curser point is dragged along the stress-strain curve is 1000 MPa, the value of the tensile strength.

(c) The approximate percent elongation corresponds to the strain at fracture multiplied by 100 (i.e., 12%) minus the maximum elastic strain (i.e., value of strain at which the linearity of the curve ends multiplied by 100—in this case about 0.5%); this gives a value of about 11.5%EL.

From Table B.4 in Appendix B, yield strength, tensile strength, and percent elongation values for the anneal Ti-6Al-4V are 830 MPa, 900 MPa, and 14%EL, while for the solution heat treated and aged alloy, the corresponding values are 1103 MPa, 1172 MPa, and 10%EL. Thus, tensile strength and percent elongation values for the *VMSE* alloy are slightly lower than for the annealed material in Table B.4 (720 vs 830 MPa, and 11.5 vs. 14 %EL), whereas the tensile strength is slightly higher (1000 vs. 900 MPa).

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6.32 *For the tempered steel alloy, whose stress strain behavior may be observed in the "Tensile Tests" module of Virtual Materials Science and Engineering (VMSE), determine the following:*

(a) the approximate yield strength (0.002 strain offset),

(b) the tensile strength, and

(c) the approximate ductility, in percent elongation.

How do these values compare with those for the oil-quenched and tempered 4140 and 4340 steel alloys presented in Table B.4 of Appendix B?

Solution

(a) It is possible to do a screen capture and then print out the entire stress-strain curve for the tempered steel alloy. The intersection of a straight line parallel to the initial linear region of the curve and offset at a strain of 0.002 with this curve is at approximately 1430 MPa.

(b) The maximum reading in the stress window located below the plot as the curser point is dragged along the stress-strain curve is 1656 MPa, the value of the tensile strength.

(c) The approximate percent elongation corresponds to the strain at fracture multiplied by 100 (i.e., 14.8%) minus the maximum elastic strain (i.e., value of strain at which the linearity of the curve ends multiplied by 100—in this case about 0.8%); this gives a value of about 14.0%EL.

For the oil-quenched and tempered 4140 and 4340 steel alloys, yield strength values presented in Table B.4 of Appendix B are 1570 MPa and 1620 MPa, respectively; these values are somewhat larger than the 1430 MPa for the tempered steel alloy of *VMSE*. Tensile strength values for these 4140 and 4340 alloys are, respectively 1720 MPa and 1760 MPa (compared to 1656 MPa for the *VMSE* steel). And, finally, the respective ductilities for the 4140 and 4340 alloys are 11.5%EL and 12%EL, which are slightly lower than the 14%EL value for the *VMSE* steel.

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6.33 *For the aluminum alloy, whose stress strain behavior may be observed in the "Tensile Tests" module of Virtual Materials Science and Engineering (VMSE), determine the following:*

(a) the approximate yield strength (0.002 strain offset),

(b) the tensile strength, and

(c) the approximate ductility, in percent elongation.

How do these values compare with those for the 2024 aluminum alloy (T351 temper) presented in Table B.4 of Appendix B?

Solution

(a) It is possible to do a screen capture and then print out the entire stress-strain curve for the aluminum alloy. The intersection of a straight line parallel to the initial linear region of the curve and offset at a strain of 0.002 with this curve is at approximately 300 MPa.

(b) The maximum reading in the stress window located below the plot as the curser point is dragged along the stress-strain curve is 484 MPa, the value of the tensile strength.

(c) The approximate percent elongation corresponds to the strain at fracture multiplied by 100 (i.e., 22.4%) minus the maximum elastic strain (i.e., value of strain at which the linearity of the curve ends multiplied by 100—in this case about 0.5%); this gives a value of about 21.9%EL.

For the 2024 aluminum alloy (T351 temper), the yield strength value presented in Table B.4 of Appendix B is 325, which is slightly larger than the 300 MPa for the aluminum alloy of *VMSE*. The tensile strength value for the 2024-T351 is 470 MPa (compared to 484 MPa for the *VMSE* alloy). And, finally, the ductility for 2024-T351 is 20%EL, which is about the same as for the *VMSE* aluminum (21.9%EL).

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6.34 *For the (plain) carbon steel alloy, whose stress strain behavior may be observed in the "Tensile Tests" module of Virtual Materials Science and Engineering (VMSE), determine the following:*

(a) the approximate yield strength,

(b) the tensile strength, and

(c) the approximate ductility, in percent elongation.

Solution

(a) It is possible to do a screen capture and then print out the entire stress-strain curve for the plain carbon steel alloy. Inasmuch as the stress-strain curve displays the yield point phenomenon, we take the yield strength as the lower yield point, which, for this steel, is about 225 MPa.

(b) The maximum reading in the stress window located below the plot as the curser point is dragged along the stress-strain curve is 274 MPa, the value of the tensile strength.

(c) The approximate percent elongation corresponds to the strain at fracture multiplied by 100 (i.e., 43.0%) minus the maximum elastic strain (i.e., value of strain at which the linearity of the curve ends multiplied by 100—in this case about 0.6%); this gives a value of about 42.4%EL.

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6.35 *A cylindrical metal specimen having an original diameter of 12.8 mm (0.505 in.) and gauge length of 50.80 mm (2.000 in.) is pulled in tension until fracture occurs. The diameter at the point of fracture is 6.60 mm (0.260 in.), and the fractured gauge length is 72.14 mm (2.840 in.). Calculate the ductility in terms of percent reduction in area and percent elongation.*

Solution

This problem calls for the computation of ductility in both percent reduction in area and percent elongation. Percent reduction in area is computed using Equation 6.12 as

$$\%\text{RA} = \frac{\pi\left(\frac{d_0}{2}\right)^2 - \pi\left(\frac{d_f}{2}\right)^2}{\pi\left(\frac{d_0}{2}\right)^2} \times 100$$

in which d_0 and d_f are, respectively, the original and fracture cross-sectional areas. Thus,

$$\%\text{RA} = \frac{\pi\left(\frac{12.8\text{ mm}}{2}\right)^2 - \pi\left(\frac{6.60\text{ mm}}{2}\right)^2}{\pi\left(\frac{12.8\text{ mm}}{2}\right)^2} \times 100 = 73.4\%$$

While, for percent elongation, we use Equation 6.11 as

$$\%\text{EL} = \left(\frac{l_f - l_0}{l_0}\right) \times 100$$

$$= \frac{72.14\text{ mm} - 50.80\text{ mm}}{50.80\text{ mm}} \times 100 = 42\%$$

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6.36 *Calculate the moduli of resilience for the materials having the stress–strain behaviors shown in Figures 6.12 and 6.21.*

Solution

This problem asks us to calculate the moduli of resilience for the materials having the stress-strain behaviors shown in Figures 6.12 and 6.21. According to Equation 6.14, the modulus of resilience U_r is a function of the yield strength and the modulus of elasticity as

$$U_r = \frac{\sigma_y^2}{2E}$$

The values for σ_y and E for the brass in Figure 6.12 are determined in Example Problem 6.3 as 250 MPa (36,000 psi) and 93.8 GPa (13.6×10^6 psi), respectively. Thus

$$U_r = \frac{(250\ \text{MPa})^2}{(2)(93.8 \times 10^3\ \text{MPa})} = 3.32 \times 10^5\ \text{J/m}^3 \quad (48.2\ \text{in.-lb}_\text{f}/\text{in.}^3)$$

Values of the corresponding parameters for the steel alloy (Figure 6.21) are determined in Problem 6.25 as 400 MPa (58,000 psi) and 200 GPa (29×10^6 psi), respectively, and therefore

$$U_r = \frac{(400\ \text{MPa})^2}{(2)(200 \times 10^3\ \text{MPa})} = 4.0 \times 10^5\ \text{J/m}^3 \quad (58\ \text{in.-lb}_\text{f}/\text{in.}^3)$$

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6.37 *Determine the modulus of resilience for each of the following alloys:*

	Yield Strength	
Material	***MPa***	***psi***
Steel alloy	*550*	*80,000*
Brass alloy	*350*	*50,750*
Aluminum alloy	*250*	*36,250*
Titanium alloy	*800*	*116,000*

Use modulus of elasticity values in Table 6.1.

Solution

The moduli of resilience of the alloys listed in the table may be determined using Equation 6.14. Yield strength values are provided in this table, whereas the elastic moduli are tabulated in Table 6.1.

For steel

$$U_r = \frac{\sigma_y^2}{2E}$$

$$= \frac{(550 \times 10^6 \text{ N/m}^2)^2}{(2)(207 \times 10^9 \text{ N/m}^2)} = 7.31 \times 10^5 \text{ J/m}^3 \quad (107 \text{ in.-lb}_f/\text{in.}^3)$$

For the brass

$$U_r = \frac{(350 \times 10^6 \text{ N/m}^2)^2}{(2)(97 \times 10^9 \text{ N/m}^2)} = 6.31 \times 10^5 \text{ J/m}^3 \quad (92.0 \text{ in.-lb}_f/\text{in.}^3)$$

For the aluminum alloy

$$U_r = \frac{(250 \times 10^6 \text{ N/m}^2)^2}{(2)(69 \times 10^9 \text{ N/m}^2)} = 4.53 \times 10^5 \text{ J/m}^3 \quad (65.7 \text{ in.-lb}_f/\text{in.}^3)$$

And, for the titanium alloy

$$U_r = \frac{(800 \times 10^6 \text{ N/m}^2)^2}{(2)(107 \times 10^9 \text{ N/m}^2)} = 30.0 \times 10^5 \text{ J/m}^3 \quad (434 \text{ in.-lb}_f/\text{in.}^3)$$

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6.38 *A brass alloy to be used for a spring application must have a modulus of resilience of at least 0.75 MPa (110 psi). What must be its minimum yield strength?*

Solution

The modulus of resilience, yield strength, and elastic modulus of elasticity are related to one another through Equation 6.14; the value of E for brass given in Table 6.1 is 97 GPa. Solving for σ_y from this expression yields

$$\sigma_y = \sqrt{2U_r E} = \sqrt{(2)(0.75\ \text{MPa})\left(97 \times 10^3\ \text{MPa}\right)}$$

$$= 381\ \text{MPa}\ \ (55{,}500\ \text{psi})$$

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True Stress and Strain

6.39 *Show that Equations 6.18a and 6.18b are valid when there is no volume change during deformation.*

Solution

To show that Equation 6.18a is valid, we must first rearrange Equation 6.17 as

$$A_i = \frac{A_0 l_0}{l_i}$$

Substituting this expression into Equation 6.15 yields

$$\sigma_T = \frac{F}{A_i} = \frac{F}{A_0}\left(\frac{l_i}{l_0}\right) = \sigma\left(\frac{l_i}{l_0}\right)$$

But, from Equation 6.2

$$\varepsilon = \frac{l_i}{l_0} - 1$$

Or

$$\frac{l_i}{l_0} = \varepsilon + 1$$

Thus,

$$\sigma_T = \sigma\left(\frac{l_i}{l_0}\right) = \sigma(\varepsilon + 1)$$

For Equation 6.18b

$$\varepsilon_T = \ln(1 + \varepsilon)$$

is valid since, from Equation 6.16

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$$\varepsilon_T = \ln\left(\frac{l_i}{l_0}\right)$$

and

$$\frac{l_i}{l_0} = \varepsilon + 1$$

from above.

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6.40 *Demonstrate that Equation 6.16, the expression defining true strain, may also be represented by*

$$\epsilon_T = \ln\left(\frac{A_0}{A_i}\right)$$

when specimen volume remains constant during deformation. Which of these two expressions is more valid during necking? Why?

Solution

This problem asks us to demonstrate that true strain may also be represented by

$$\epsilon_T = \ln\left(\frac{A_0}{A_i}\right)$$

Rearrangement of Equation 6.17 leads to

$$\frac{l_i}{l_0} = \frac{A_0}{A_i}$$

Thus, Equation 6.16 takes the form

$$\epsilon_T = \ln\left(\frac{l_i}{l_0}\right) = \ln\left(\frac{A_0}{A_i}\right)$$

The expression $\epsilon_T = \ln\left(\frac{A_0}{A_i}\right)$ is more valid during necking because A_i is taken as the area of the neck.

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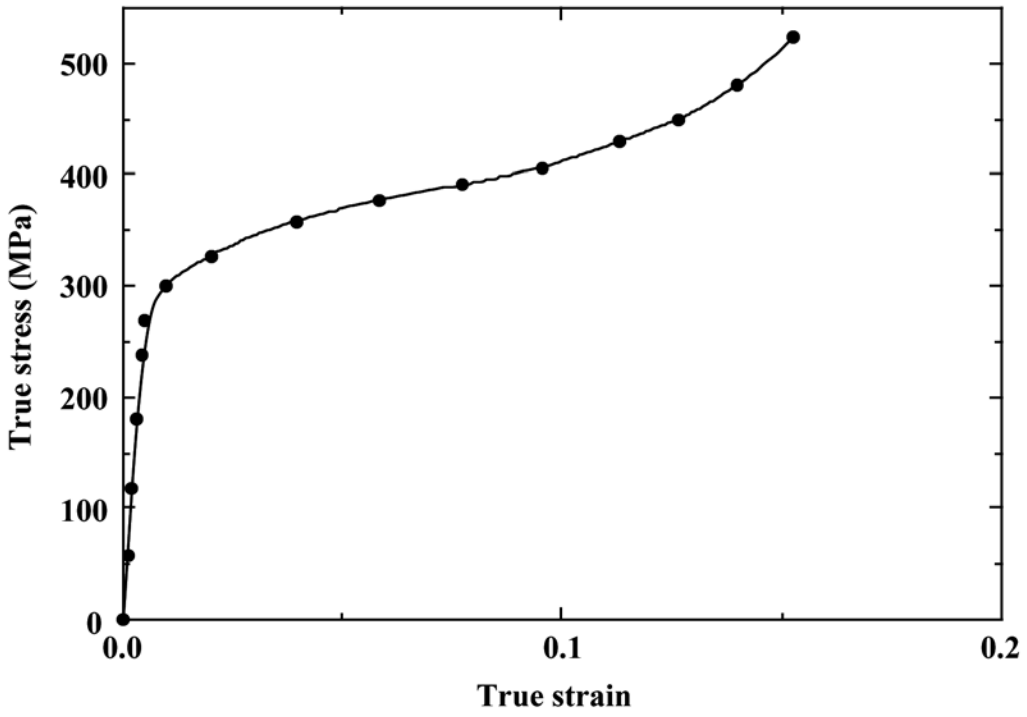
6.41 *Using the data in Problem 6.28 and Equations 6.15, 6.16, and 6.18a, generate a true stress–true strain plot for aluminum. Equation 6.18a becomes invalid past the point at which necking begins; therefore, measured diameters are given below for the last four data points, which should be used in true stress computations.*

Load		***Length***		***Diameter***	
N	***lb_f***	***mm***	***in.***	***mm***	***in.***
46,100	*10,400*	*56.896*	*2.240*	*11.71*	*0.461*
42,400	*10,100*	*57.658*	*2.270*	*10.95*	*0.431*
42,600	*9,600*	*58.420*	*2.300*	*10.62*	*0.418*
36,400	*8,200*	*59.182*	*2.330*	*9.40*	*0.370*

Solution

These true stress-strain data are plotted below.



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6.42 *A tensile test is performed on a metal specimen, and it is found that a true plastic strain of 0.20 is produced when a true stress of 575 MPa (83,500 psi) is applied; for the same metal, the value of K in Equation 6.19 is 860 MPa (125,000 psi). Calculate the true strain that results from the application of a true stress of 600 MPa (87,000 psi).*

Solution

It first becomes necessary to solve for n in Equation 6.19. Taking logarithms of this expression and after rearrangement we have

$$n = \frac{\log \sigma_T - \log K}{\log \varepsilon_T}$$

And, incorporating values of the parameters provided in the problem statement leads to

$$n = \frac{\log (575 \text{ MPa}) - \log (860 \text{ MPa})}{\log (0.20)} = 0.250$$

Expressing ε_T as the dependent variable (Equation 6.19), and then solving for its value from the data stipulated in the problem statement, leads to

$$\varepsilon_T = \left(\frac{\sigma_T}{K}\right)^{1/n} = \left(\frac{600 \text{ MPa}}{860 \text{ MPa}}\right)^{1/0.250} = 0.237$$

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6.43 *For some metal alloy, a true stress of 415 MPa (60,175 psi) produces a plastic true strain of 0.475. How much will a specimen of this material elongate when a true stress of 325 MPa (46,125 psi) is applied if the original length is 300 mm (11.8 in.)? Assume a value of 0.25 for the strain-hardening exponent n.*

Solution

Solution of this problem requires that we utilize Equation 6.19. It is first necessary to solve for K from the given true stress and strain. Rearrangement of this equation yields

$$K = \frac{\sigma_T}{(\varepsilon_T)^n} = \frac{415\ \text{MPa}}{(0.475)^{0.25}} = 500\ \text{MPa}\quad (72{,}500\ \text{psi})$$

Next we must solve for the true strain produced when a true stress of 325 MPa is applied, also using Equation 6.19. Thus

$$\varepsilon_T = \left(\frac{\sigma_T}{K}\right)^{1/n} = \left(\frac{325\ \text{MPa}}{500\ \text{MPa}}\right)^{1/0.25} = 0.179 = \ln\left(\frac{l_i}{l_0}\right)$$

Now, solving for l_i gives

$$l_i = l_0 e^{0.179} = (300\ \text{mm})\, e^{0.179} = 358.8\ \text{mm}\ \ (14.11\ \text{in.})$$

And finally, the elongation Δl is just

$$\Delta l = l_i - l_0 = 358.8\ \text{mm} - 300\ \text{mm} = 58.8\ \text{mm}\ \ (2.31\ \text{in.})$$

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6.44 T*he following true stresses produce the corresponding true plastic strains for a brass alloy:*

True Stress (psi)	***True Strain***
50,000	*0.10*
60,000	*0.20*

What true stress is necessary to produce a true plastic strain of 0.25?

Solution

For this problem, we are given two values of ε_T and σ_T, from which we are asked to calculate the true stress which produces a true plastic strain of 0.25. Employing Equation 6.19, we may set up two simultaneous equations with two unknowns (the unknowns being K and n), as

$$\log (50,000 \text{ psi}) = \log K + n \log (0.10)$$

$$\log (60,000 \text{ psi}) = \log K + n \log (0.20)$$

Solving for n from these two expressions yields

$$n = \frac{\log (50,000) - \log (60,000)}{\log (0.10) - \log (0.20)} = 0.263$$

and for K

$$\log K = 4.96 \text{ or } K = 10^{4.96} = 91,623 \text{ psi}$$

Thus, for $\varepsilon_T = 0.25$

$$\sigma_T = K (\varepsilon_T)^n = (91,623 \text{ psi})(0.25)^{0.263} = 63,700 \text{ psi} \quad (440 \text{ MPa})$$

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6.45 *For a brass alloy, the following engineering stresses produce the corresponding plastic engineering strains, prior to necking:*

Engineering Stress (MPa)	***Engineering Strain***
235	*0.194*
250	*0.296*

On the basis of this information, compute the engineering *stress necessary to produce an* engineering *strain of 0.25.*

Solution

For this problem we first need to convert engineering stresses and strains to true stresses and strains so that the constants K and n in Equation 6.19 may be determined. Since $\sigma_T = \sigma(1 + \varepsilon)$ then

$$\sigma_{T1} = (235\ \text{MPa})(1 + 0.194) = 280\ \text{MPa}$$

$$\sigma_{T2} = (250\ \text{MPa})(1 + 0.296) = 324\ \text{MPa}$$

Similarly for strains, since $\varepsilon_T = \ln(1 + \varepsilon)$ then

$$\varepsilon_{T1} = \ln\ (1\ + 0.194) = 0.177$$

$$\varepsilon_{T2} = \ln\ (1\ +\ 0.296) = 0.259$$

Taking logarithms of Equation 6.19, we get

$$\log \sigma_T\ = \log K\ +\ n \log \varepsilon_T$$

which allows us to set up two simultaneous equations for the above pairs of true stresses and true strains, with K and n as unknowns. Thus

$$\log\ (280) = \log K\ +\ n \log\ (0.177)$$

$$\log\ (324) = \log K\ +\ n \log\ (0.259)$$

Solving for these two expressions yields $K = 543$ MPa and $n = 0.383$.

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Now, converting $\varepsilon = 0.25$ to true strain

$$\varepsilon_T = \ln (1 + 0.25) = 0.223$$

The corresponding σ_T to give this value of ε_T (using Equation 6.19) is just

$$\sigma_T = K\varepsilon_T^n = (543 \text{ MPa})(0.223)^{0.383} = 306 \text{ MPa}$$

Now converting this value of σ_T to an engineering stress using Equation 6.18a gives

$$\sigma = \frac{\sigma_T}{1 + \varepsilon} = \frac{306 \text{ MPa}}{1 + 0.25} = 245 \text{ MPa}$$

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6.46 *Find the toughness (or energy to cause fracture) for a metal that experiences both elastic and plastic deformation. Assume Equation 6.5 for elastic deformation, that the modulus of elasticity is 172 GPa (25×10^6 psi), and that elastic deformation terminates at a strain of 0.01. For plastic deformation, assume that the relationship between stress and strain is described by Equation 6.19, in which the values for K and n are 6900 MPa (1×10^6 psi) and 0.30, respectively. Furthermore, plastic deformation occurs between strain values of 0.01 and 0.75, at which point fracture occurs*.

Solution

This problem calls for us to compute the toughness (or energy to cause fracture). The easiest way to do this is to integrate both elastic and plastic regions, and then add them together.

$$\text{Toughness} = \int \sigma \, d\varepsilon$$

$$= \int_0^{0.01} E\varepsilon \, d\varepsilon + \int_{0.01}^{0.75} K\varepsilon^n \, d\varepsilon$$

$$= \left. \frac{E\varepsilon^2}{2} \right|_0^{0.01} + \left. \frac{K}{(n+1)} \varepsilon^{(n+1)} \right|_{0.01}^{0.75}$$

$$= \frac{172 \times 10^9 \text{ N/m}^2}{2} (0.01)^2 + \frac{6900 \times 10^6 \text{ N/m}^2}{(1.0 + 0.3)} \left[(0.75)^{1.3} - (0.01)^{1.3} \right]$$

$$= 3.65 \times 10^9 \text{ J/m}^3 \ \left(5.29 \times 10^5 \text{ in.-lb}_f/\text{in.}^3 \right)$$

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6.47 *For a tensile test, it can be demonstrated that necking begins when*

$$\frac{d\sigma_T}{d\varepsilon_T} = \sigma_T \tag{6.26}$$

Using Equation 6.19, determine the value of the true strain at this onset of necking.

Solution

Let us take the derivative of Equation 6.19, set it equal to σ_T, and then solve for ε_T from the resulting expression. Thus

$$\frac{d\left[K(\varepsilon_T)^n\right]}{d\varepsilon_T} = Kn(\varepsilon_T)^{(n-1)} = \sigma_T$$

However, from Equation 6.19, $\sigma_T = K(\varepsilon_T)^n$, which, when substituted into the above expression, yields

$$Kn(\varepsilon_T)^{(n\,-\,1)} = K(\varepsilon_T)^n$$

Now solving for ε_T from this equation leads to

$$\varepsilon_T = n$$

as the value of the true strain at the onset of necking.

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6.48 *Taking the logarithm of both sides of Equation 6.19 yields*

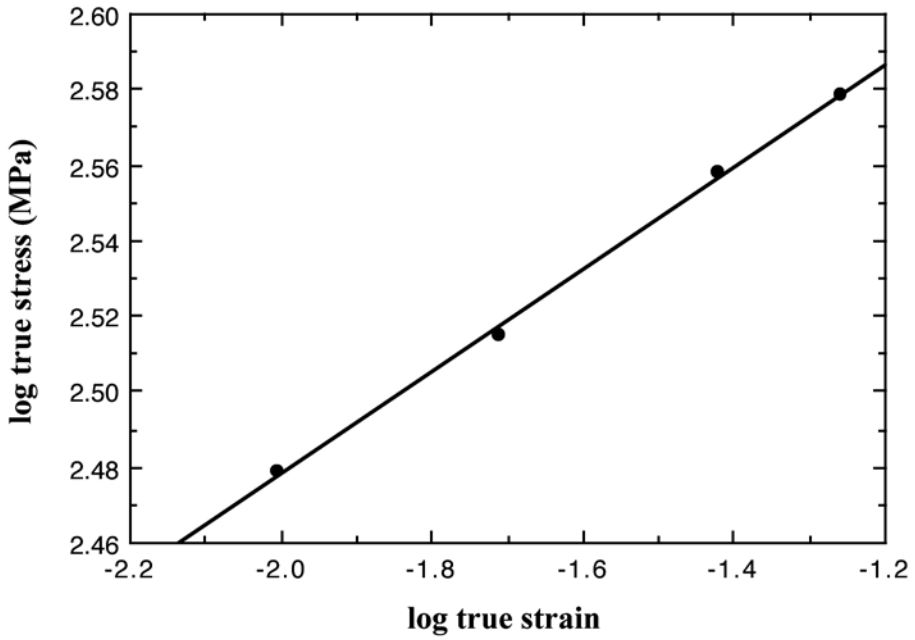
$$\log \sigma_T = \log K + n \log \in_T \qquad (6.27)$$

Thus, a plot of log σ_T versus log $\in_T$ in the plastic region to the point of necking should yield a straight line having a slope of n and an intercept (at log σ_T = 0) of log K.

Using the appropriate data tabulated in Problem 6.29, make a plot of log σ_T versus log $\in_T$ and determine the values of n and K. It will be necessary to convert engineering stresses and strains to true stresses and strains using Equations 6.18a and 6.18b.

Solution

This problem calls for us to utilize the appropriate data from Problem 6.29 in order to determine the values of *n* and *K* for this material. From Equation 6.27 the slope and intercept of a log σ_T versus log ε_T plot will yield *n* and log *K*, respectively. However, Equation 6.19 is only valid in the region of plastic deformation to the point of necking; thus, only the 7th, 8th, 9th, and 10th data points may be utilized. The log-log plot with these data points is given below.



The slope yields a value of 0.136 for *n*, whereas the intercept gives a value of 2.7497 for log *K*, and thus $K = 10^{2.7497} = 562$ MPa.

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Elastic Recovery After Plastic Deformation

6.49 *A cylindrical specimen of a brass alloy 7.5 mm (0.30 in.) in diameter and 90.0 mm (3.54 in.) long is pulled in tension with a force of 6000 N (1350 lb_f); the force is subsequently released.*

(a) Compute the final length of the specimen at this time. The tensile stress–strain behavior for this alloy is shown in Figure 6.12.

(b) Compute the final specimen length when the load is increased to 16,500 N (3700 lb_f) and then released.

Solution

(a) In order to determine the final length of the brass specimen when the load is released, it first becomes necessary to compute the applied stress using Equation 6.1; thus

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{6000\ \text{N}}{\pi\left(\frac{7.5 \times 10^{-3}\ \text{m}}{2}\right)^2} = 136\ \text{MPa}\ \ (19{,}000\ \text{psi})$$

Upon locating this point on the stress-strain curve (Figure 6.12), we note that it is in the linear, elastic region; therefore, when the load is released the specimen will return to its original length of 90 mm (3.54 in.).

(b) In this portion of the problem we are asked to calculate the final length, after load release, when the load is increased to 16,500 N (3700 lb_f). Again, computing the stress

$$\sigma = \frac{16{,}500\ \text{N}}{\pi\left(\frac{7.5 \times 10^{-3}\ \text{m}}{2}\right)^2} = 373\ \text{MPa}\ \ (52{,}300\ \text{psi})$$

The point on the stress-strain curve corresponding to this stress is in the plastic region. We are able to estimate the amount of permanent strain by drawing a straight line parallel to the linear elastic region; this line intersects the strain axis at a strain of about 0.08 which is the amount of plastic strain. The final specimen length l_i may be determined from a rearranged form of Equation 6.2 as

$$l_i = l_0(1 + \varepsilon) = (90\ \text{mm})(1 + 0.08) = 97.20\ \text{mm}\ (3.82\ \text{in.})$$

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6.50 *A steel alloy specimen having a rectangular cross section of dimensions 12.7 mm × 6.4 mm (0.5 in. × 0.25 in.) has the stress–strain behavior shown in Figure 6.21. If this specimen is subjected to a tensile force of 38,000 N (8540 lb$_f$) then*

(a) Determine the elastic and plastic strain values.

(b) If its original length is 460 mm (18.0 in.), what will be its final length after the load in part (a) is applied and then released?

Solution

(a) We are asked to determine both the elastic and plastic strain values when a tensile force of 38,000 N (8540 lb$_f$) is applied to the steel specimen and then released. First it becomes necessary to determine the applied stress using Equation 6.1; thus

$$\sigma = \frac{F}{A_0} = \frac{F}{b_0 d_0}$$

where b_0 and d_0 are cross-sectional width and depth (12.7 mm and 6.4 mm, respectively). Thus

$$\sigma = \frac{38{,}000\ \text{N}}{(12.7 \times 10^{-3}\ \text{m})(6.4 \times 10^{-3}\ \text{m})} = 468 \times 10^6\ \text{N/m}^2 = 468\ \text{MPa}\ \ (68{,}300\ \text{psi})$$

From Figure 6.21, this point is in the plastic region so the specimen will be both elastic and plastic strains. The total strain at this point, ε_t, is about 0.010. We are able to estimate the amount of permanent strain recovery ε_e from Hooke's law, Equation 6.5 as

$$\varepsilon_e = \frac{\sigma}{E}$$

And, since E = 207 GPa for steel (Table 6.1)

$$\varepsilon_e = \frac{468\ \text{MPa}}{207 \times 10^3\ \text{MPa}} = 0.00226$$

The value of the plastic strain, ε_p is just the difference between the total and elastic strains; that is

$$\varepsilon_p = \varepsilon_t - \varepsilon_e = 0.010 - 0.00226 = 0.00774$$

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(b) If the initial length is 460 mm (18.0 in.) then the final specimen length l_i may be determined from a rearranged form of Equation 6.2 using the plastic strain value as

$$l_i = l_0(1 + \varepsilon_p) = (460 \text{ mm})(1 + 0.00774) = 463.6 \text{ mm } (18.14 \text{ in.})$$

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Hardness

6.51 *(a) A 10-mm-diameter Brinell hardness indenter produced an indentation 1.62 mm in diameter in a steel alloy when a load of 500 kg was used. Compute the HB of this material.*

(b) What will be the diameter of an indentation to yield a hardness of 450 HB when a 500 kg load is used?

Solution

(a) We are asked to compute the Brinell hardness for the given indentation. It is necessary to use the equation in Table 6.5 for HB, where P = 500 kg, d = 1.62 mm, and D = 10 mm. Thus, the Brinell hardness is computed as

$$\text{HB} = \frac{2P}{\pi D\left[D - \sqrt{D^2 - d^2}\right]}$$

$$= \frac{(2)(500\text{ kg})}{(\pi)(10\text{ mm})\left[10\text{ mm} - \sqrt{(10\text{ mm})^2 - (1.62\text{ mm})^2}\right]} = 241$$

(b) This part of the problem calls for us to determine the indentation diameter d which will yield a 450 HB when P = 500 kg. Solving for d from the equation in Table 6.5 gives

$$d = \sqrt{D^2 - \left[D - \frac{2P}{(\text{HB})\pi D}\right]^2}$$

$$= \sqrt{(10\text{mm})^2 - \left[10\text{ mm} - \frac{(2)(500\text{ kg})}{(450)(\pi)(10\text{ mm})}\right]^2} = 1.19\text{ mm}$$

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6.52 *Estimate the Brinell and Rockwell hardnesses for the following:*

(a) The naval brass for which the stress–strain behavior is shown in Figure 6.12.

(b) The steel alloy for which the stress–strain behavior is shown in Figure 6.21.

Solution

This problem calls for estimations of Brinell and Rockwell hardnesses.

(a) For the brass specimen, the stress-strain behavior for which is shown in Figure 6.12, the tensile strength is 450 MPa (65,000 psi). From Figure 6.19, the hardness for brass corresponding to this tensile strength is about 125 HB or 70 HRB.

(b) The steel alloy (Figure 6.21) has a tensile strength of about 515 MPa (74,700 psi) [Problem 6.25(d)]. This corresponds to a hardness of about 160 HB or ~90 HRB from the line for steels in Figure 6.19. Alternately, using Equation 6.20a

$$\text{HB} = \frac{TS(\text{MPa})}{3.45} = \frac{515\ \text{MPa}}{3.45} = 149$$

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6.53 *Using the data represented in Figure 6.19, specify equations relating tensile strength and Brinell hardness for brass and nodular cast iron, similar to Equations 6.20a and 6.20b for steels.*

Solution

These equations, for a straight line, are of the form

$$TS = C + (E)(\text{HB})$$

where TS is the tensile strength, HB is the Brinell hardness, and C and E are constants, which need to be determined.

One way to solve for C and E is analytically--establishing two equations using TS and HB data points on the plot, as

$$(TS)_1 = C + (E)(\text{BH})_1$$
$$(TS)_2 = C + (E)(\text{BH})_2$$

Solving for E from these two expressions yields

$$E = \frac{(TS)_1 - (TS)_2}{(\text{HB})_2 - (\text{HB})_1}$$

For nodular cast iron, if we make the arbitrary choice of $(\text{HB})_1$ and $(\text{HB})_2$ as 200 and 300, respectively, then, from Figure 6.19, $(TS)_1$ and $(TS)_2$ take on values of 600 MPa (87,000 psi) and 1100 MPa (160,000 psi), respectively. Substituting these values into the above expression and solving for E gives

$$E = \frac{600 \text{ MPa} - 1100 \text{ MPa}}{200 \text{ HB} - 300 \text{ HB}} = 5.0 \text{ MPa/HB} \quad (730 \text{ psi/HB})$$

Now, solving for C yields

$$C = (TS)_1 - (E)(\text{BH})_1$$

$$= 600 \text{ MPa} - (5.0 \text{ MPa/HB})(200 \text{ HB}) = -400 \text{ MPa} \; (-59{,}000 \text{ psi})$$

Thus, for nodular cast iron, these two equations take the form

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$$TS(\text{MPa}) = -400 + 5.0 \times \text{HB}$$
$$TS(\text{psi}) = -59{,}000 + 730 \times \text{HB}$$

Now for brass, we take $(\text{HB})_1$ and $(\text{HB})_2$ as 100 and 200, respectively, then, from Figure 7.31, $(TS)_1$ and $(TS)_2$ take on values of 370 MPa (54,000 psi) and 660 MPa (95,000 psi), respectively. Substituting these values into the above expression and solving for E gives

$$E = \frac{370\ \text{MPa} - 660\ \text{MPa}}{100\ \text{HB} - 200\ \text{HB}} = 2.9\ \text{MPa/HB}\ \ (410\ \text{psi/HB})$$

Now, solving for C yields

$$C = (TS)_1 - (E)(\text{BH})_1$$

$$= 370\ \text{MPa} - (2.9\ \text{MPa/HB})(100\ \text{HB}) = 80\ \text{MPa}\ \ (13{,}000\ \text{psi})$$

Thus, for brass these two equations take the form

$$TS(\text{MPa}) = 80 + 2.9 \times \text{HB}$$
$$TS(\text{psi}) = 13{,}000 + 410 \times \text{HB}$$

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Variability of Material Properties

6.54 *Cite five factors that lead to scatter in measured material properties.*

Solution

The five factors that lead to scatter in measured material properties are the following: (1) test method; (2) variation in specimen fabrication procedure; (3) operator bias; (4) apparatus calibration; and (5) material inhomogeneities and/or compositional differences.

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6.55 *Below are tabulated a number of Rockwell B hardness values that were measured on a single steel specimen. Compute average and standard deviation hardness values.*

83.3	*80.7*	*86.4*
88.3	*84.7*	*85.2*
82.8	*87.8*	*86.9*
86.2	*83.5*	*84.4*
87.2	*85.5*	*86.3*

Solution

The average of the given hardness values is calculated using Equation 6.21 as

$$\overline{\text{HRB}} = \frac{\sum_{i=1}^{15} \text{HRB}_i}{15}$$

$$= \frac{83.3 + 88.3 + 82.8 \ldots . + 86.3}{15} = 85.3$$

And we compute the standard deviation using Equation 6.22 as follows:

$$s = \sqrt{\frac{\sum_{i=1}^{15} \left(\text{HRB}_i - \overline{\text{HRB}}\right)^2}{15 - 1}}$$

$$= \left[\frac{(83.3 - 85.3)^2 + (88.3 - 85.3)^2 + \ldots . + (86.3 - 85.3)^2}{14}\right]^{1/2}$$

$$= \sqrt{\frac{60.31}{14}} = 2.08$$

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Design/Safety Factors

6.56 *Upon what three criteria are factors of safety based?*

Solution

The criteria upon which factors of safety are based are (1) consequences of failure, (2) previous experience, (3) accuracy of measurement of mechanical forces and/or material properties, and (4) economics.

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6.57 *Determine working stresses for the two alloys that have the stress–strain behaviors shown in Figures 6.12 and 6.21.*

Solution

The working stresses for the two alloys the stress-strain behaviors of which are shown in Figures 6.12 and 6.21 are calculated by dividing the yield strength by a factor of safety, which we will take to be 2. For the brass alloy (Figure 6.12), since σ_y = 250 MPa (36,000 psi), the working stress is 125 MPa (18,000 psi), whereas for the steel alloy (Figure 6.21), σ_y = 400 MPa (58,000 psi), and, therefore, σ_w = 200 MPa (29,000 psi).

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DESIGN PROBLEMS

6.D1 *A large tower is to be supported by a series of steel wires. It is estimated that the load on each wire will be 11,100 N (2500 lb_f). Determine the minimum required wire diameter assuming a factor of safety of 2 and a yield strength of 1030 MPa (150,000 psi).*

Solution

For this problem the working stress is computed using Equation 6.24 with $N = 2$, as

$$\sigma_w = \frac{\sigma_y}{2} = \frac{1030 \text{ MPa}}{2} = 515 \text{ MPa} \quad (75{,}000 \text{ psi})$$

Since the force is given, the area may be determined from Equation 6.1, and subsequently the original diameter d_0 may be calculated as

$$A_0 = \frac{F}{\sigma_w} = \pi\left(\frac{d_0}{2}\right)^2$$

And

$$d_0 = \sqrt{\frac{4F}{\pi\sigma_w}} = \sqrt{\frac{(4)(11{,}100 \text{ N})}{\pi\left(515 \times 10^6 \text{ N/m}^2\right)}}$$

$$= 5.23 \times 10^{-3} \text{ m} = 5.23 \text{ mm } (0.206 \text{ in.})$$

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6.D2 *(a) Gaseous hydrogen at a constant pressure of 1.013 MPa (10 atm) is to flow within the inside of a thin-walled cylindrical tube of nickel that has a radius of 0.1 m. The temperature of the tube is to be 300°C and the pressure of hydrogen outside of the tube will be maintained at 0.01013 MPa (0.1 atm). Calculate the minimum wall thickness if the diffusion flux is to be no greater than* 1×10^{-7} *mol/m*^{2}*-s. The concentration of hydrogen in the nickel,* C_H *(in moles hydrogen per m*^{3} *of Ni) is a function of hydrogen pressure,* P_{H_2} *(in MPa) and absolute temperature (T) according to*

$$C_{\mathrm{H}} = 30.8\sqrt{p_{\mathrm{H_2}}}\,\exp\left(-\frac{12.3\ \mathrm{kJ/mol}}{RT}\right) \qquad (6.28)$$

Furthermore, the diffusion coefficient for the diffusion of H in Ni depends on temperature as

$$D_{\mathrm{H}} = 4.76 \times 10^{-7}\exp\left(-\frac{39.56\ \mathrm{kJ/mol}}{RT}\right) \qquad (6.29)$$

(b) For thin-walled cylindrical tubes that are pressurized, the circumferential stress is a function of the pressure difference across the wall (Δp), cylinder radius (r), and tube thickness (Δx) as

$$\sigma = \frac{r\,\Delta p}{4\,\Delta x} \qquad (6.30)$$

Compute the circumferential stress to which the walls of this pressurized cylinder are exposed.

(c) The room-temperature yield strength of Ni is 100 MPa (15,000 psi) and, furthermore, σ_y *diminishes about 5 MPa for every 50°C rise in temperature. Would you expect the wall thickness computed in part (b) to be suitable for this Ni cylinder at 300°C? Why or why not?*

(d) If this thickness is found to be suitable, compute the minimum thickness that could be used without any deformation of the tube walls. How much would the diffusion flux increase with this reduction in thickness? On the other hand, if the thickness determined in part (c) is found to be unsuitable, then specify a minimum thickness that you would use. In this case, how much of a diminishment in diffusion flux would result?

Solution

(a) This portion of the problem asks for us to compute the wall thickness of a thin-walled cylindrical Ni tube at 300°C through which hydrogen gas diffuses. The inside and outside pressures are, respectively, 1.1013 and 0.01013 MPa, and the diffusion flux is to be no greater than 1×10^{-7} mol/m^2-s. This is a steady-state diffusion problem, which necessitates that we employ Equation 5.3. The concentrations at the inside and outside wall faces may be determined using Equation 6.28, and, furthermore, the diffusion coefficient is computed using Equation 6.29. Solving for Δx (using Equation 5.3)

$$\Delta x = -\frac{D\,\Delta C}{J}$$

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$$= - \frac{1}{1 \times 10^{-7}\ \text{mol/m}^2 - \text{s}} \times$$

$$\left(4.76 \times 10^{-7}\right) \exp\left(-\frac{39{,}560\ \text{J/mol}}{(8.31\ \text{J/mol - K})(300 + 273\ \text{K})}\right) \times$$

$$(30.8) \exp\left(-\frac{12{,}300\ \text{J/mol}}{(8.31\ \text{J/mol - K})(300 + 273\ \text{K})}\right)\left(\sqrt{0.01013\ \text{MPa}} - \sqrt{1.1013\ \text{MPa}}\right)$$

$$= 0.0025\ \text{m} = 2.5\ \text{mm}$$

(b) Now we are asked to determine the circumferential stress:

$$\sigma = \frac{r\,\Delta p}{4\,\Delta x}$$

$$= \frac{(0.10\ \text{m})(1.013\ \text{MPa} - 0.01013\ \text{MPa})}{(4)(0.0025\ \text{m})}$$

$$= 10.0\ \text{MPa}$$

(c) Now we are to compare this value of stress to the yield strength of Ni at 300°C, from which it is possible to determine whether or not the 2.5 mm wall thickness is suitable. From the information given in the problem, we may write an equation for the dependence of yield strength (σ_y) on temperature (T) as follows:

$$\sigma_y = 100\ \text{MPa} - \frac{5\ \text{MPa}}{50°\text{C}}\left(T - T_r\right)$$

where T_r is room temperature and for temperature in degrees Celsius. Thus, at 300°C

$$\sigma_y = 100\ \text{MPa} - (0.1\ \text{MPa/°C})\,(300°\text{C} - 20°\text{C}) = 72\ \text{MPa}$$

Inasmuch as the circumferential stress (10 MPa) is much less than the yield strength (72 MPa), this thickness is entirely suitable.

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(d) And, finally, this part of the problem asks that we specify how much this thickness may be reduced and still retain a safe design. Let us use a working stress by dividing the yield stress by a factor of safety, according to Equation 6.24. On the basis of our experience, let us use a value of 2.0 for *N*. Thus

$$\sigma_w = \frac{\sigma_y}{N} = \frac{72\ \text{MPa}}{2} = 36\ \text{MPa}$$

Using this value for σ_w and Equation 6.30, we now compute the tube thickness as

$$\Delta x = \frac{r\,\Delta p}{4\sigma_w}$$

$$= \frac{(0.10\ \text{m})(1.013\ \text{MPa} - 0.01013\ \text{MPa})}{4(36\ \text{MPa})}$$

$$= 0.00070\ \text{m} = 0.70\ \text{mm}$$

Substitution of this value into Fick's first law we calculate the diffusion flux as follows:

$$J = -D\frac{\Delta C}{\Delta x}$$

$$= -\left(4.76 \times 10^{-7}\right)\exp\left[-\frac{39{,}560\ \text{J/mol}}{(8.31\ \text{J/mol-K})(300 + 273\ \text{K})}\right] \times$$

$$\frac{(30.8)\exp\left[-\dfrac{12{,}300\ \text{J/mol}}{(8.31\ \text{J/mol-K})(300 + 273\ \text{K})}\right]\left(\sqrt{0.01013\ \text{MPa}} - \sqrt{1.013\ \text{MPa}}\right)}{0.0007\ \text{m}}$$

$$= 3.53 \times 10^{-7}\ \text{mol/m}^2\text{-s}$$

Thus, the flux increases by approximately a factor of 3.5, from 1×10^{-7} to 3.53×10^{-7} mol/m^2-s with this reduction in thickness.

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6.D3 *Consider the steady-state diffusion of hydrogen through the walls of a cylindrical nickel tube as described in Problem 6.D2. One design calls for a diffusion flux of* 5×10^{-8} *mol/m*^{2}*-s, a tube radius of 0.125 m, and inside and outside pressures of 2.026 MPa (20 atm) and 0.0203 MPa (0.2 atm), respectively; the maximum allowable temperature is 450°C. Specify a suitable temperature and wall thickness to give this diffusion flux and yet ensure that the tube walls will not experience any permanent deformation.*

Solution

This problem calls for the specification of a temperature and cylindrical tube wall thickness that will give a diffusion flux of 5×10^{-8} mol/m^2-s for the diffusion of hydrogen in nickel; the tube radius is 0.125 m and the inside and outside pressures are 2.026 and 0.0203 MPa, respectively. There are probably several different approaches that may be used; and, of course, there is not one unique solution. Let us employ the following procedure to solve this problem: (1) assume some wall thickness, and, then, using Fick's first law for diffusion (which also employs Equations 5.3 and 6.29), compute the temperature at which the diffusion flux is that required; (2) compute the yield strength of the nickel at this temperature using the dependence of yield strength on temperature as stated in Problem 6.D2; (3) calculate the circumferential stress on the tube walls using Equation 6.30; and (4) compare the yield strength and circumferential stress values--the yield strength should probably be at least twice the stress in order to make certain that no permanent deformation occurs. If this condition is not met then another iteration of the procedure should be conducted with a more educated choice of wall thickness.

As a starting point, let us arbitrarily choose a wall thickness of 2 mm (2×10^{-3} m). The steady-state diffusion equation, Equation 5.3, takes the form

$$J = -D\frac{\Delta C}{\Delta x}$$

$$= 5 \times 10^{-8} \text{ mol/m}^2\text{-s}$$

$$= -\left(4.76 \times 10^{-7}\right)\exp\left[-\frac{39{,}560 \text{ J/mol}}{(8.31 \text{ J/mol - K})(T)}\right] \times$$

$$\frac{(30.8)\exp\left[-\frac{12{,}300 \text{ J/mol}}{(8.31 \text{ J/mol - K})(T)}\right]\left(\sqrt{0.0203 \text{ MPa}} - \sqrt{2.026 \text{ MPa}}\right)}{0.002 \text{ m}}$$

Solving this expression for the temperature T gives $T = 514$ K = 241°C; this value is satisfactory inasmuch as it is less than the maximum allowable value (450°C).

The next step is to compute the stress on the wall using Equation 6.30; thus

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$$\sigma = \frac{r\,\Delta p}{4\,\Delta x}$$

$$= \frac{(0.125\ \text{m})(2.026\ \text{MPa} - 0.0203\ \text{MPa})}{(4)\left(2 \times 10^{-3}\ \text{m}\right)}$$

$$= 31.3\ \text{MPa}$$

Now, the yield strength (σ_y) of Ni at this temperature may be computed using the expression

$$\sigma_y = 100\ \text{MPa} - \frac{5\ \text{MPa}}{50°\text{C}}\left(T - T_r\right)$$

where T_r is room temperature. Thus,

$$\sigma_y = 100\ \text{MPa} - (0.1\ \text{MPa/°C})(241°\text{C} - 20°\text{C}) = 77.9\ \text{MPa}$$

Inasmuch as this yield strength is greater than twice the circumferential stress, wall thickness and temperature values of 2 mm and 241°C are satisfactory design parameters.

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CHAPTER 7

DISLOCATIONS AND STRENGTHENING MECHANISMS

PROBLEM SOLUTIONS

Basic Concepts of Dislocations
Characteristics of Dislocations

7.1 *To provide some perspective on the dimensions of atomic defects, consider a metal specimen that has a dislocation density of 10^4 mm^{-2}. Suppose that all the dislocations in 1000 mm^3 (1 cm^3) were somehow removed and linked end to end. How far (in miles) would this chain extend? Now suppose that the density is increased to 10^{10} mm^{-2} by cold working. What would be the chain length of dislocations in 1000 mm^3 of material?*

Solution

The dislocation density is just the total dislocation length per unit volume of material (in this case per cubic millimeters). Thus, the total length in 1000 mm^3 of material having a density of 10^4 mm^{-2} is just

$$\left(10^4 \text{ mm}^{-2}\right)\left(1000 \text{ mm}^3\right) = 10^7 \text{ mm} = 10^4 \text{ m} = 6.2 \text{ mi}$$

Similarly, for a dislocation density of 10^{10} mm^{-2}, the total length is

$$\left(10^{10} \text{ mm}^{-2}\right)\left(1000 \text{ mm}^3\right) = 10^{13} \text{ mm} = 10^{10} \text{ m} = 6.2 \times 10^6 \text{ mi}$$

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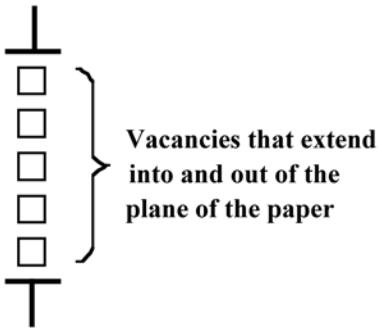
7.2 *Consider two edge dislocations of opposite sign and having slip planes that are separated by several atomic distances as indicated in the diagram. Briefly describe the defect that results when these two dislocations become aligned with each other.*

Solution

When the two edge dislocations become aligned, a planar region of vacancies will exist between the dislocations as:



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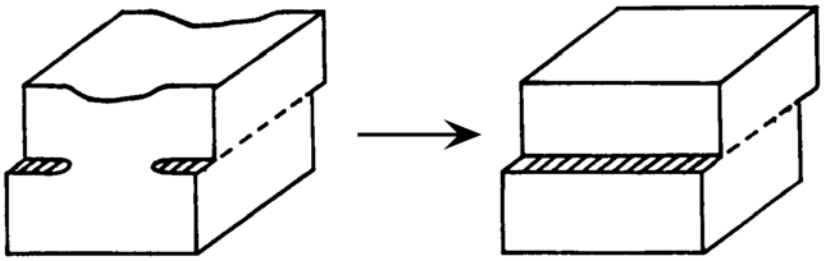
7.3 *Is it possible for two screw dislocations of opposite sign to annihilate each other? Explain your answer.*

Solution

It is possible for two screw dislocations of opposite sign to annihilate one another if their dislocation lines are parallel. This is demonstrated in the figure below.



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7.4 *For each of edge, screw, and mixed dislocations, cite the relationship between the direction of the applied shear stress and the direction of dislocation line motion.*

Solution

For the various dislocation types, the relationships between the direction of the applied shear stress and the direction of dislocation line motion are as follows:

edge dislocation--parallel

screw dislocation--perpendicular

mixed dislocation--neither parallel nor perpendicular

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Slip Systems

7.5 *(a) Define a slip system.*

(b) Do all metals have the same slip system? Why or why not?

Solution

(a) A slip system is a crystallographic plane, and, within that plane, a direction along which dislocation motion (or slip) occurs.

(b) All metals do not have the same slip system. The reason for this is that for most metals, the slip system will consist of the most densely packed crystallographic plane, and within that plane the most closely packed direction. This plane and direction will vary from crystal structure to crystal structure.

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7.6 *(a) Compare planar densities (Section 3.11 and Problem 3.54) for the (100), (110), and (111) planes for FCC.*

(b) Compare planar densities (Problem 3.55) for the (100), (110), and (111) planes for BCC.

Solution

(a) For the FCC crystal structure, the planar density for the (110) plane is given in Equation 3.11 as

$$PD_{110}(FCC) = \frac{1}{4R^2\sqrt{2}} = \frac{0.177}{R^2}$$

Furthermore, the planar densities of the (100) and (111) planes are calculated in Homework Problem 3.54, which are as follows:

$$PD_{100}(FCC) = \frac{1}{4R^2} = \frac{0.25}{R^2}$$

$$PD_{111}(FCC) = \frac{1}{2R^2\sqrt{3}} = \frac{0.29}{R^2}$$

(b) For the BCC crystal structure, the planar densities of the (100) and (110) planes were determined in Homework Problem 3.55, which are as follows:

$$PD_{100}(BCC) = \frac{3}{16R^2} = \frac{0.19}{R^2}$$

$$PD_{110}(BCC) = \frac{3}{8R^2\sqrt{2}} = \frac{0.27}{R^2}$$

Below is a BCC unit cell, within which is shown a (111) plane.

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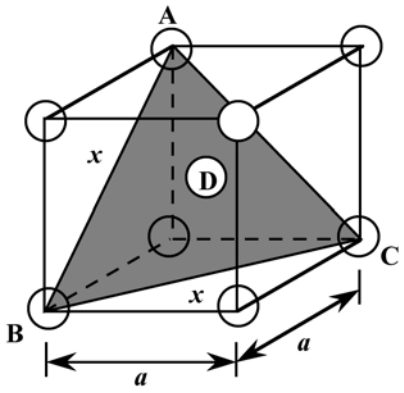
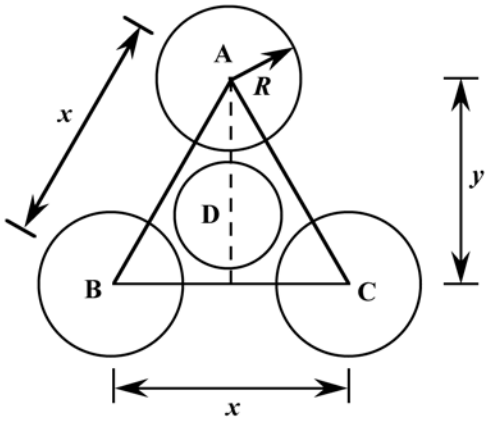


(*a*)

The centers of the three corner atoms, denoted by A, B, and C lie on this plane. Furthermore, the (111) plane does not pass through the center of atom D, which is located at the unit cell center. The atomic packing of this plane is presented in the following figure; the corresponding atom positions from the Figure (*a*) are also noted.



(*b*)

Inasmuch as this plane does not pass through the center of atom D, it is not included in the atom count. One sixth of each of the three atoms labeled A, B, and C is associated with this plane, which gives an equivalence of one-half atom.

In Figure (*b*) the triangle with A, B, and C at its corners is an equilateral triangle. And, from Figure (*b*), the area of this triangle is $\frac{xy}{2}$. The triangle edge length, x, is equal to the length of a face diagonal, as indicated in Figure (*a*). And its length is related to the unit cell edge length, a, as

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$$x^2 = a^2 + a^2 = 2a^2$$

or

$$x = a\sqrt{2}$$

For BCC, $a = \dfrac{4R}{\sqrt{3}}$ (Equation 3.3), and, therefore,

$$x = \frac{4R\sqrt{2}}{\sqrt{3}}$$

Also, from Figure (*b*), with respect to the length y we may write

$$y^2 + \left(\frac{x}{2}\right)^2 = x^2$$

which leads to $y = \dfrac{x\sqrt{3}}{2}$. And, substitution for the above expression for x yields

$$y = \frac{x\sqrt{3}}{2} = \left(\frac{4R\sqrt{2}}{\sqrt{3}}\right)\left(\frac{\sqrt{3}}{2}\right) = \frac{4R\sqrt{2}}{2}$$

Thus, the area of this triangle is equal to

$$\text{AREA} = \frac{1}{2}xy = \left(\frac{1}{2}\right)\left(\frac{4R\sqrt{2}}{\sqrt{3}}\right)\left(\frac{4R\sqrt{2}}{2}\right) = \frac{8R^2}{\sqrt{3}}$$

And, finally, the planar density for this (111) plane is

$$\text{PD}_{111}(\text{BCC}) = \frac{0.5 \text{ atom}}{\dfrac{8R^2}{\sqrt{3}}} = \frac{\sqrt{3}}{16R^2} = \frac{0.11}{R^2}$$

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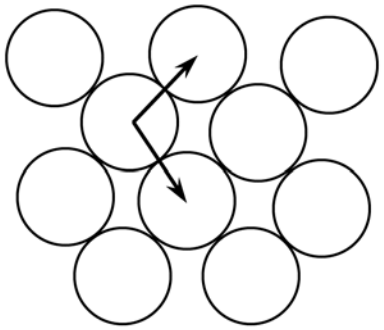
7.7 *One slip system for the BCC crystal structure is* $\{110\}\langle 111\rangle$. *In a manner similar to Figure 7.6b, sketch a* $\{110\}$*-type plane for the BCC structure, representing atom positions with circles. Now, using arrows, indicate two different* $\langle 111\rangle$ *slip directions within this plane.*

Solution

Below is shown the atomic packing for a BCC $\{110\}$-type plane. The arrows indicate two different $\langle 111\rangle$-type directions.



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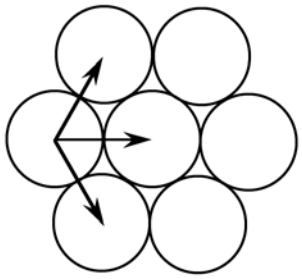
7.8 *One slip system for the HCP crystal structure is* $\{0001\}\langle 11\bar{2}0\rangle$. *In a manner similar to Figure 7.6b, sketch a* $\{0001\}$*-type plane for the HCP structure and, using arrows, indicate three different* $\langle 11\bar{2}0\rangle$ *slip directions within this plane. You might find Figure 3.8 helpful.*

Solution

Below is shown the atomic packing for an HCP $\{0001\}$-type plane. The arrows indicate three different $\langle 11\bar{2}0\rangle$-type directions.



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7.9 *Equations 7.1a and 7.1b, expressions for Burgers vectors for FCC and BCC crystal structures, are of the form*

$$\mathbf{b} = \frac{a}{2}\langle uvw \rangle$$

where a is the unit cell edge length. Also, since the magnitudes of these Burgers vectors may be determined from the following equation:

$$|\mathbf{b}| = \frac{a}{2}\left(u^2 + v^2 + w^2\right)^{1/2} \qquad (7.10)$$

*determine values of |**b**| for aluminum and chromium. You may want to consult Table 3.1.*

Solution

For Al, which has an FCC crystal structure, R = 0.1431 nm (Table 3.1) and $a = 2R\sqrt{2}$ = 0.4047 nm (Equation 3.1); also, from Equation 7.1a, the Burgers vector for FCC metals is

$$\mathbf{b} = \frac{a}{2}\langle 110 \rangle$$

Therefore, the values for u, v, and w in Equation 7.10 are 1, 1, and 0, respectively. Hence, the magnitude of the Burgers vector for Al is

$$|\mathbf{b}| = \frac{a}{2}\sqrt{u^2 + v^2 + w^2}$$

$$= \frac{0.4047 \text{ nm}}{2}\sqrt{(1)^2 + (1)^2 + (0)^2} = 0.2862 \text{ nm}$$

For Cr which has a BCC crystal structure, R = 0.1249 nm (Table 3.1) and $a = \frac{4R}{\sqrt{3}}$ = 0.2884 nm (Equation 3.3); also, from Equation 7.1b, the Burgers vector for BCC metals is

$$\mathbf{b} = \frac{a}{2}\langle 111 \rangle$$

Therefore, the values for u, v, and w in Equation 7.10 are 1, 1, and 1, respectively. Hence, the magnitude of the Burgers vector for Cr is

$$|\mathbf{b}| = \frac{0.2884 \text{ nm}}{2}\sqrt{(1)^2 + (1)^2 + (1)^2} = 0.2498 \text{ nm}$$

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7.10 *(a) In the manner of Equations 7.1a, 7.1b, and 7.1c, specify the Burgers vector for the simple cubic crystal structure. Its unit cell is shown in Figure 3.24. Also, simple cubic is the crystal structure for the edge dislocation of Figure 4.3, and for its motion as presented in Figure 7.1. You may also want to consult the answer to Concept Check 7.1.*

(b) On the basis of Equation 7.10, formulate an expression for the magnitude of the Burgers vector, $|\boldsymbol{b}|$, for simple cubic.

Solution

(a) This part of the problem asks that we specify the Burgers vector for the simple cubic crystal structure (and suggests that we consult the answer to Concept Check 7.1). This Concept Check asks that we select the slip system for simple cubic from four possibilities. The correct answer is $\{100\}\langle 010\rangle$. Thus, the Burgers vector will lie in a $\langle 010\rangle$-type direction. Also, the unit slip distance is a (i.e., the unit cell edge length, Figures 4.3 and 7.1). Therefore, the Burgers vector for simple cubic is

$$\mathbf{b} = a\langle 010\rangle$$

Or, equivalently

$$\mathbf{b} = a\langle 100\rangle$$

(b) The magnitude of the Burgers vector, $|\mathbf{b}|$, for simple cubic is

$$|\mathbf{b}| = a(1^2 + 0^2 + 0^2)^{1/2} = a$$

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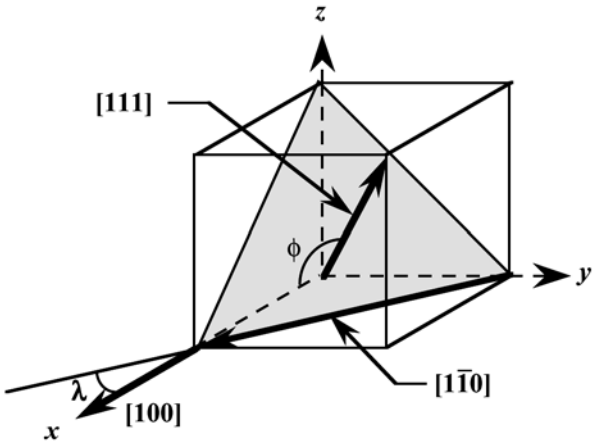
Slip in Single Crystals

7.11 *Sometimes cos ϕ cos λ in Equation 7.2 is termed the Schmid factor. Determine the magnitude of the Schmid factor for an FCC single crystal oriented with its* [*100*] *direction parallel to the loading axis.*

Solution

We are asked to compute the *Schmid factor* for an FCC crystal oriented with its [100] direction parallel to the loading axis. With this scheme, slip may occur on the (111) plane and in the $[1\bar{1}0]$ direction as noted in the figure below.



The angle between the [100] and $[1\bar{1}0]$ directions, λ, may be determined using Equation 7.6

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [100]) $u_1 = 1$, $v_1 = 0$, $w_1 = 0$, and (for $[1\bar{1}0]$) $u_2 = 1$, $v_2 = -1$, $w_2 = 0$. Therefore, λ is equal to

$$\lambda = \cos^{-1}\left[\frac{(1)(1) + (0)(-1) + (0)(0)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (-1)^2 + (0)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

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Now, the angle ϕ is equal to the angle between the normal to the (111) plane (which is the [111] direction), and the [100] direction. Again from Equation 7.6, and for $u_1 = 1$, $v_1 = 1$, $w_1 = 1$, and $u_2 = 1$, $v_2 = 0$, and $w_2 = 0$, we have

$$\phi = \cos^{-1}\left| \frac{(1)(1) + (1)(0) + (1)(0)}{\sqrt{\left[(1)^2 + (1)^2 + (1)^2\right]\left[(1)^2 + (0)^2 + (0)^2\right]}} \right|$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{3}}\right) = 54.7^\circ$$

Therefore, the Schmid factor is equal to

$$\cos\lambda \cos\phi = \cos(45^\circ)\cos(54.7^\circ) = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{3}}\right) = 0.408$$

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7.12 *Consider a metal single crystal oriented such that the normal to the slip plane and the slip direction are at angles of 43.1° and 47.9°, respectively, with the tensile axis. If the critical resolved shear stress is 20.7 MPa (3000 psi), will an applied stress of 45 MPa (6500 psi) cause the single crystal to yield? If not, what stress will be necessary?*

Solution

This problem calls for us to determine whether or not a metal single crystal having a specific orientation and of given critical resolved shear stress will yield. We are given that $\phi = 43.1°$, $\lambda = 47.9°$, and that the values of the critical resolved shear stress and applied tensile stress are 20.7 MPa (3000 psi) and 45 MPa (6500 psi), respectively. From Equation 7.2

$$\tau_R = \sigma \cos\phi \cos\lambda = (45 \text{ MPa})(\cos 43.1°)(\cos 47.9°) = 22.0 \text{ MPa} \quad (3181 \text{ psi})$$

Since the resolved shear stress (22 MPa) is greater than the critical resolved shear stress (20.7 MPa), the single crystal will yield.

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7.13 *A single crystal of aluminum is oriented for a tensile test such that its slip plane normal makes an angle of 28.1° with the tensile axis. Three possible slip directions make angles of 62.4°, 72.0°, and 81.1° with the same tensile axis.*

(a) Which of these three slip directions is most favored?

(b) If plastic deformation begins at a tensile stress of 1.95 MPa (280 psi), determine the critical resolved shear stress for aluminum.

Solution

We are asked to compute the critical resolved shear stress for Al. As stipulated in the problem, $\phi = 28.1°$, while possible values for λ are 62.4°, 72.0°, and 81.1°.

(a) Slip will occur along that direction for which ($\cos\phi \cos\lambda$) is a maximum, or, in this case, for the largest $\cos\lambda$. Cosines for the possible λ values are given below.

$$\cos(62.4°) = 0.46$$
$$\cos(72.0°) = 0.31$$
$$\cos(81.1°) = 0.15$$

Thus, the slip direction is at an angle of 62.4° with the tensile axis.

(b) From Equation 7.4, the critical resolved shear stress is just

$$\tau_{crss} = \sigma_y (\cos\phi \cos\lambda)_{max}$$

$$= (1.95 \text{ MPa})\left[\cos(28.1°)\cos(62.4°)\right] = 0.80 \text{ MPa} \quad (114 \text{ psi})$$

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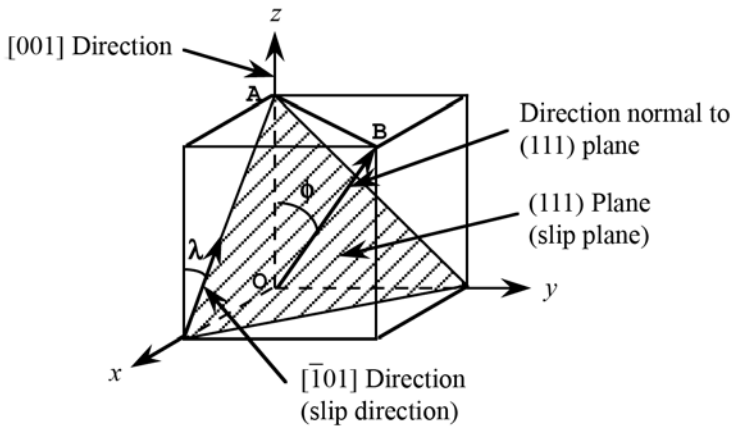
7.14 *Consider a single crystal of silver oriented such that a tensile stress is applied along a [001] direction. If slip occurs on a (111) plane and in a $[\bar{1}01]$ direction, and is initiated at an applied tensile stress of 1.1 MPa (160 psi), compute the critical resolved shear stress.*

Solution

This problem asks that we compute the critical resolved shear stress for silver. In order to do this, we must employ Equation 7.4, but first it is necessary to solve for the angles λ and ϕ which are shown in the sketch below.



The angle λ is the angle between the tensile axis—i.e., along the [001] direction—and the slip direction—i.e., $[\bar{1}01]$. The angle λ may be determined using Equation 7.6 as

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [001]) $u_1 = 0$, $v_1 = 0$, $w_1 = 1$, and (for $[\bar{1}01]$) $u_2 = -1$, $v_2 = 0$, $w_2 = 1$. Therefore, λ is equal to

$$\lambda = \cos^{-1}\left[\frac{(0)(-1) + (0)(0) + (1)(1)}{\sqrt{\left[(0)^2 + (0)^2 + (1)^2\right]\left[(-1)^2 + (0)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

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Furthermore, ϕ is the angle between the tensile axis—the [001] direction—and the normal to the slip plane—i.e., the (111) plane; for this case this normal is along a [111] direction. Therefore, again using Equation 7.6

$$\phi = \cos^{-1}\left[\frac{(0)(1) + (0)(1) + (1)(1)}{\sqrt{\left[(0)^2 + (0)^2 + (1)^2\right]\left[(1)^2 + (1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{3}}\right) = 54.7°$$

And, finally, using Equation 7.4, the critical resolved shear stress is equal to

$$\tau_{crss} = \sigma_y (\cos\phi \cos\lambda)$$

$$= (1.1 \text{ MPa})\left[\cos(54.7°)\cos(45°)\right] = (1.1 \text{ MPa})\left(\frac{1}{\sqrt{3}}\right)\left(\frac{1}{\sqrt{2}}\right) = 0.45 \text{ MPa} \quad (65.1 \text{ psi})$$

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7.15 *A single crystal of a metal that has the FCC crystal structure is oriented such that a tensile stress is applied parallel to the* [*110*] *direction. If the critical resolved shear stress for this material is 1.75 MPa, calculate the magnitude(s) of applied stress(es) necessary to cause slip to occur on the* (*111*) *plane in each of the* $[1\bar{1}0]$, $[10\bar{1}]$ *and* $[01\bar{1}]$ *directions.*

Solution

In order to solve this problem it is necessary to employ Equation 7.4, but first we need to solve for the for λ and ϕ angles for the three slip systems.

For each of these three slip systems, the ϕ will be the same—i.e., the angle between the direction of the applied stress, [110] and the normal to the (111) plane, that is, the [111] direction. The angle ϕ may be determined using Equation 7.6 as

$$\phi = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [110]) $u_1 = 1$, $v_1 = 1$, $w_1 = 0$, and (for [111]) $u_2 = 1$, $v_2 = 1$, $w_2 = 1$. Therefore, ϕ is equal to

$$\phi = \cos^{-1}\left[\frac{(1)(1) + (1)(1) + (0)(1)}{\sqrt{\left[(1)^2 + (1)^2 + (0)^2\right]\left[(1)^2 + (1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{2}{\sqrt{6}}\right) = 35.3°$$

Let us now determine λ for the $[1\bar{1}0]$ slip direction. Again, using Equation 7.6 where $u_1 = 1$, $v_1 = 1$, $w_1 = 0$ (for [110]), and $u_2 = 1$, $v_2 = -1$, $w_2 = 0$ (for $[1\bar{1}0]$. Therefore, λ is determined as

$$\lambda_{[110]-[1\bar{1}0]} = \cos^{-1}\left[\frac{(1)(1) + (1)(-1) + (0)(0)}{\sqrt{\left[(1)^2 + (1)^2 + (0)^2\right]\left[(1)^2 + (-1)^2 + (0)^2\right]}}\right]$$

$$= \cos^{-1} 0 = 90°$$

Now, we solve for the yield strength for this (111)–$[1\bar{1}0]$ slip system using Equation 7.4 as

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$$\sigma_y = \frac{\tau_{crss}}{(\cos\phi\ \cos\lambda)}$$

$$= \frac{1.75\ \text{MPa}}{\cos(35.3°)\ \cos(90°)} = \frac{1.75\ \text{MPa}}{(0.816)(0)} = \infty$$

which means that slip will not occur on this (111)–$[1\bar{1}0]$ slip system.

Now, we must determine the value of λ for the (111)–$[10\bar{1}]$ slip system—that is, the angle between the $[110]$ and $[10\bar{1}]$ directions. Again using Equation 7.6

$$\lambda_{[110]-[10\bar{1}]} = \cos^{-1}\left[\frac{(1)(1) + (1)(0) + (0)(-1)}{\sqrt{\left[(1)^2 + (1)^2 + (0)^2\right]\left[(1)^2 + (0)^2 + (-1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{2}\right) = 60°$$

Now, we solve for the yield strength for this (111)–$[10\bar{1}]$ slip system using Equation 7.4 as

$$\sigma_y = \frac{\tau_{crss}}{(\cos\phi\ \cos\lambda)}$$

$$= \frac{1.75\ \text{MPa}}{\cos(35.3°)\ \cos(60°)} = \frac{1.75\ \text{MPa}}{(0.816)(0.500)} = 4.29\ \text{MPa}$$

And, finally, for the (111)–$[01\bar{1}]$ slip system, λ is computed using Equation 7.6 as follows:

$$\lambda_{[110]-[01\bar{1}]} = \cos^{-1}\left[\frac{(1)(0) + (1)(1) + (0)(-1)}{\sqrt{\left[(1)^2 + (1)^2 + (0)^2\right]\left[(0)^2 + (1)^2 + (-1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{2}\right) = 60°$$

Thus, since the values of ϕ and λ for this (110)–$[01\bar{1}]$ slip system are the same as for (111)–$[10\bar{1}]$, so also will σ_y be the same—viz 4.29 MPa.

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7.16 *(a) A single crystal of a metal that has the BCC crystal structure is oriented such that a tensile stress is applied in the* [*010*] *direction. If the magnitude of this stress is 2.75 MPa, compute the resolved shear stress in the* $[\bar{1}\,11]$ *direction on each of the* (*110*) *and* (*101*) *planes.*

(b) On the basis of these resolved shear stress values, which slip system(s) is (are) most favorably oriented?

Solution

(a) This part of the problem asks, for a BCC metal, that we compute the resolved shear stress in the $[\bar{1}\,11]$ direction on each of the (110) and (101) planes. In order to solve this problem it is necessary to employ Equation 7.2, which means that we first need to solve for the for angles λ and ϕ for the three slip systems.

For each of these three slip systems, the λ will be the same—i.e., the angle between the direction of the applied stress, [010] and the slip direction, $[\bar{1}\,11]$. This angle λ may be determined using Equation 7.6

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [010]) $u_1 = 0$, $v_1 = 1$, $w_1 = 0$, and (for $[\bar{1}\,11]$) $u_2 = -1$, $v_2 = 1$, $w_2 = 1$. Therefore, λ is determined as

$$\lambda = \cos^{-1}\left[\frac{(0)(-1) + (1)(1) + (0)(1)}{\sqrt{\left[(0)^2 + (1)^2 + (0)^2\right]\left[(-1)^2 + (1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{3}}\right) = 54.7°$$

Let us now determine ϕ for the angle between the direction of the applied tensile stress—i.e., the [010] direction—and the normal to the (110) slip plane—i.e., the [110] direction. Again, using Equation 7.6 where $u_1 = 0$, $v_1 = 1$, $w_1 = 0$ (for [010]), and $u_2 = 1$, $v_2 = 1$, $w_2 = 0$ (for [110]), ϕ is equal to

$$\phi_{[010]-[110]} = \cos^{-1}\left[\frac{(0)(1) + (1)(1) + (0)(0)}{\sqrt{\left[(0)^2 + (1)^2 + (0)^2\right]\left[(1)^2 + (1)^2 + (0)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

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Now, using Equation 7.2

$$\tau_R = \sigma \cos\phi \cos\lambda$$

we solve for the resolved shear stress for this slip system as

$$\tau_{R(110)-[\bar{1}11]} = (2.75\ \text{MPa})\left[\cos(54.7°)\cos(45°)\right] = (2.75\ \text{MPa})(0.578)(0.707) = 1.12\ \text{MPa}$$

Now, we must determine the value of ϕ for the $(101)-[\bar{1}11]$ slip system—that is, the angle between the direction of the applied stress, [010], and the normal to the (101) plane—i.e., the [101] direction. Again using Equation 7.6

$$\lambda_{[010]-[101]} = \cos^{-1}\left[\frac{(0)(1) + (1)(0) + (0)(1)}{\sqrt{\left[(0)^2 + (1)^2 + (0)^2\right]\left[(1)^2 + (0)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}(0) = 90°$$

Thus, the resolved shear stress for this $(101)-[\bar{1}11]$ slip system is

$$\tau_{R(101)-[\bar{1}11]} = = (2.75\ \text{MPa})\left[\cos(54.7°)\cos(90°)\right] = (2.75\ \text{MPa})(0.578)(0) = 0\ \text{MPa}$$

(b) The most favored slip system(s) is (are) the one(s) that has (have) the largest τ_R value. Therefore, the $(110)-[\bar{1}11]$ is the most favored since its τ_R (1.12 MPa) is greater than the τ_R value for $(101)-[\bar{1}11]$ (viz., 0 MPa).

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7.17 *Consider a single crystal of some hypothetical metal that has the FCC crystal structure and is oriented such that a tensile stress is applied along a* $[\bar{1}02]$ *direction. If slip occurs on a* (111) *plane and in a* $[\bar{1}01]$ *direction, compute the stress at which the crystal yields if its critical resolved shear stress is 3.42 MPa.*

Solution

This problem asks for us to determine the tensile stress at which a FCC metal yields when the stress is applied along a $[\bar{1}02]$ direction such that slip occurs on a (111) plane and in a $[\bar{1}01]$ direction; the critical resolved shear stress for this metal is 3.42 MPa. To solve this problem we use Equation 7.4; however it is first necessary to determine the values of ϕ and λ. These determinations are possible using Equation 7.6. Now, λ is the angle between $[\bar{1}02]$ and $[\bar{1}01]$ directions. Therefore, relative to Equation 7.6 let us take $u_1 = -1$, $v_1 = 0$, and $w_1 = 2$, as well as $u_2 = -1$, $v_2 = 0$, and $w_2 = 1$. This leads to

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

$$= \cos^{-1}\left\{\frac{(-1)(-1) + (0)(0) + (2)(1)}{\sqrt{\left[(-1)^2 + (0)^2 + (2)^2\right]\left[(-1)^2 + (0)^2 + (1)^2\right]}}\right\}$$

$$= \cos^{-1}\left(\frac{3}{\sqrt{10}}\right) = 18.4°$$

Now for the determination of ϕ, the normal to the (111) slip plane is the [111] direction. Again using Equation 7.6, where we now take $u_1 = -1$, $v_1 = 0$, $w_1 = 2$ (for $[\bar{1}02]$), and $u_2 = 1$, $v_2 = 1$, $w_2 = 1$ (for [111]). Thus,

$$\phi = \cos^{-1}\left\{\frac{(-1)(1) + (0)(1) + (2)(1)}{\sqrt{\left[(-1)^2 + (0)^2 + (2)^2\right]\left[(1)^2 + (1)^2 + (1)^2\right]}}\right\}$$

$$= \cos^{-1}\left(\frac{3}{\sqrt{15}}\right) = 39.2°$$

It is now possible to compute the yield stress (using Equation 7.4) as

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$$\sigma_y = \frac{\tau_{crss}}{\cos\phi\ \cos\lambda} = \frac{3.42\ \text{MPa}}{\left(\frac{3}{\sqrt{10}}\right)\left(\frac{3}{\sqrt{15}}\right)} = 4.65\ \text{MPa}$$

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7.18 *The critical resolved shear stress for iron is 27 MPa (4000 psi). Determine the maximum possible yield strength for a single crystal of Fe pulled in tension.*

Solution

In order to determine the maximum possible yield strength for a single crystal of Fe pulled in tension, we simply employ Equation 7.5 as

$$\sigma_y = 2\tau_{crss} = (2)(27\ \text{MPa}) = 54\ \text{MPa}\quad (8000\ \text{psi})$$

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Deformation by Twinning

7.19 *List four major differences between deformation by twinning and deformation by slip relative to mechanism, conditions of occurrence, and final result.*

Solution

Four major differences between deformation by twinning and deformation by slip are as follows: (1) with slip deformation there is no crystallographic reorientation, whereas with twinning there is a reorientation; (2) for slip, the atomic displacements occur in atomic spacing multiples, whereas for twinning, these displacements may be other than by atomic spacing multiples; (3) slip occurs in metals having many slip systems, whereas twinning occurs in metals having relatively few slip systems; and (4) normally slip results in relatively large deformations, whereas only small deformations result for twinning.

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Strengthening by Grain Size Reduction

7.20 *Briefly explain why small-angle grain boundaries are not as effective in interfering with the slip process as are high-angle grain boundaries.*

Solution

Small-angle grain boundaries are not as effective in interfering with the slip process as are high-angle grain boundaries because there is not as much crystallographic misalignment in the grain boundary region for small-angle, and therefore not as much change in slip direction.

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7.21 *Briefly explain why HCP metals are typically more brittle than FCC and BCC metals.*

Solution

Hexagonal close packed metals are typically more brittle than FCC and BCC metals because there are fewer slip systems in HCP.

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7.22 *Describe in your own words the three strengthening mechanisms discussed in this chapter (i.e., grain size reduction, solid-solution strengthening, and strain hardening). Be sure to explain how dislocations are involved in each of the strengthening techniques.*

These three strengthening mechanisms are described in Sections 7.8, 7.9, and 7.10.

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7.23 *(a) From the plot of yield strength versus (grain diameter)$^{-1/2}$ for a 70 Cu–30 Zn cartridge brass, Figure 7.15, determine values for the constants σ_0 and k_y in Equation 7.7.*

(b) Now predict the yield strength of this alloy when the average grain diameter is 1.0×10^{-3} mm.

Solution

(a) Perhaps the easiest way to solve for σ_0 and k_y in Equation 7.7 is to pick two values each of σ_y and $d^{-1/2}$ from Figure 7.15, and then solve two simultaneous equations, which may be created. For example

$d^{-1/2}$ (mm)$^{-1/2}$	σ_y (MPa)
4	75
12	175

The two equations are thus

$$75 = \sigma_0 + 4k_y$$

$$175 = \sigma_0 + 12k_y$$

Solution of these equations yield the values of

$$k_y = 12.5 \text{ MPa}(\text{mm})^{1/2} \quad \left[1810 \text{ psi}(\text{mm})^{1/2}\right]$$

$$\sigma_0 = 25 \text{ MPa} \quad (3630 \text{ psi})$$

(b) When $d = 1.0 \times 10^{-3}$ mm, $d^{-1/2} = 31.6$ mm$^{-1/2}$, and, using Equation 7.7,

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$

$$= (25 \text{ MPa}) + \left[12.5 \text{ MPa}(\text{mm})^{1/2}\right]\left(31.6 \text{ mm}^{-1/2}\right) = 420 \text{ MPa} \quad (61,000 \text{ psi})$$

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7.24 *The lower yield point for an iron that has an average grain diameter of 5×10^{-2} mm is 135 MPa (19,500 psi). At a grain diameter of 8×10^{-3} mm, the yield point increases to 260 MPa (37,500 psi). At what grain diameter will the lower yield point be 205 MPa (30,000 psi)?*

Solution

The best way to solve this problem is to first establish two simultaneous expressions of Equation 7.7, solve for σ_0 and k_y, and finally determine the value of d when $\sigma_y = 205$ MPa. The data pertaining to this problem may be tabulated as follows:

σ_y	d (mm)	$d^{-1/2}$ $(\text{mm})^{-1/2}$
135 MPa	5×10^{-2}	4.47
260 MPa	8×10^{-3}	11.18

The two equations thus become

$$135 \text{ MPa} = \sigma_0 + (4.47)\, k_y$$

$$260 \text{ MPa} = \sigma_0 + (11.18)\, k_y$$

Which yield the values, $\sigma_0 = 51.7$ MPa and $k_y = 18.63$ MPa$(\text{mm})^{1/2}$. At a yield strength of 205 MPa

$$205 \text{ MPa} = 51.7 \text{ MPa} + \left[18.63 \text{ MPa}\,(\text{mm})^{1/2}\right] d^{-1/2}$$

or $d^{-1/2} = 8.23\ (\text{mm})^{-1/2}$, which gives $d = 1.48 \times 10^{-2}$ mm.

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7.25 *If it is assumed that the plot in Figure 7.15 is for noncold-worked brass, determine the grain size of the alloy in Figure 7.19; assume its composition is the same as the alloy in Figure 7.15.*

Solution

This problem asks that we determine the grain size of the brass for which is the subject of Figure 7.19. From Figure 7.19*a*, the yield strength of brass at 0%CW is approximately 175 MPa (26,000 psi). This yield strength from Figure 7.15 corresponds to a $d^{-1/2}$ value of approximately 12.0 $(\text{mm})^{-1/2}$. Thus, $d = 6.9 \times 10^{-3}$ mm.

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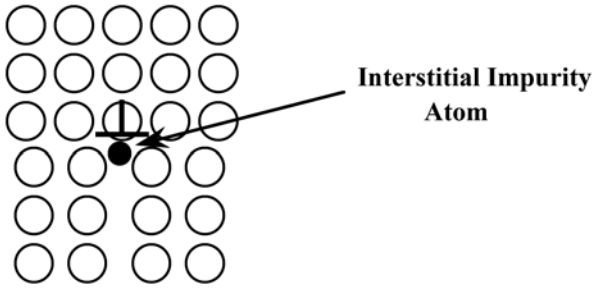
Solid-Solution Strengthening

7.26 *In the manner of Figures 7.17b and 7.18b, indicate the location in the vicinity of an edge dislocation at which an interstitial impurity atom would be expected to be situated. Now briefly explain in terms of lattice strains why it would be situated at this position.*

Solution

Below is shown an edge dislocation and where an interstitial impurity atom would be located. Compressive lattice strains are introduced by the impurity atom. There will be a net reduction in lattice strain energy when these lattice strains partially cancel tensile strains associated with the edge dislocation; such tensile strains exist just below the bottom of the extra half-plane of atoms (Figure 7.4).



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Strain Hardening

7.27 *(a) Show, for a tensile test, that*

$$\%CW = \left(\frac{\varepsilon}{\varepsilon + 1}\right) \times 100$$

if there is no change in specimen volume during the deformation process (i.e., $A_0 l_0 = A_d l_d$).

(b) Using the result of part (a), compute the percent cold work experienced by naval brass (the stress-strain behavior of which is shown in Figure 6.12) when a stress of 400 MPa (58,000 psi) is applied.

Solution

(a) From Equation 7.8

$$\%CW = \left(\frac{A_0 - A_d}{A_0}\right) \times 100 = \left(1 - \frac{A_d}{A_0}\right) \times 100$$

Which is also equal to

$$\left(1 - \frac{l_0}{l_d}\right) \times 100$$

since $A_d/A_0 = l_0/l_d$, the conservation of volume stipulation given in the problem statement. Now, from the definition of engineering strain (Equation 6.2)

$$\varepsilon = \frac{l_d - l_0}{l_0} = \frac{l_d}{l_0} - 1$$

Or,

$$\frac{l_0}{l_d} = \frac{1}{\varepsilon + 1}$$

Substitution for l_0 / l_d into the %CW expression above gives

$$\%CW = \left(1 - \frac{l_0}{l_d}\right) \times 100 = \left(1 - \frac{1}{\varepsilon + 1}\right) \times 100 = \left(\frac{\varepsilon}{\varepsilon + 1}\right) \times 100$$

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(b) From Figure 6.12, a stress of 400 MPa (58,000 psi) corresponds to a strain of 0.13. Using the above expression

$$\%CW = \left(\frac{\varepsilon}{\varepsilon + 1}\right) \times 100 = \left(\frac{0.13}{0.13 + 1.00}\right) \times 100 = 11.5\%CW$$

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7.28 *Two previously undeformed cylindrical specimens of an alloy are to be strain hardened by reducing their cross-sectional areas (while maintaining their circular cross sections). For one specimen, the initial and deformed radii are 16 mm and 11 mm, respectively. The second specimen, with an initial radius of 12 mm, must have the same deformed hardness as the first specimen; compute the second specimen's radius after deformation.*

Solution

In order for these two cylindrical specimens to have the same deformed hardness, they must be deformed to the same percent cold work. For the first specimen

$$\%CW = \frac{A_0 - A_d}{A_0} \times 100 = \frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2} \times 100$$

$$= \frac{\pi (16 \text{ mm})^2 - \pi (11 \text{ mm})^2}{\pi (16 \text{ mm})^2} \times 100 = 52.7\%CW$$

For the second specimen, the deformed radius is computed using the above equation and solving for r_d as

$$r_d = r_0 \sqrt{1 - \frac{\%CW}{100}}$$

$$= (12 \text{ mm}) \sqrt{1 - \frac{52.7\%CW}{100}} = 8.25 \text{ mm}$$

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7.29 *Two previously undeformed specimens of the same metal are to be plastically deformed by reducing their cross-sectional areas. One has a circular cross section, and the other is rectangular; during deformation the circular cross section is to remain circular, and the rectangular is to remain as such. Their original and deformed dimensions are as follows:*

	Circular (diameter, mm)	***Rectangular (mm)***
Original dimensions	*15.2*	*125 × 175*
Deformed dimensions	*11.4*	*75 × 200*

Which of these specimens will be the hardest after plastic deformation, and why?

Solution

The hardest specimen will be the one that has experienced the greatest degree of cold work. Therefore, all we need do is to compute the %CW for each specimen using Equation 7.8. For the circular one

$$\%\text{CW} = \left[\frac{A_0 - A_d}{A_0}\right] \times 100$$

$$= \left[\frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2}\right] \times 100$$

$$= \left[\frac{\pi\left(\frac{15.2\text{ mm}}{2}\right)^2 - \pi\left(\frac{11.4\text{ mm}}{2}\right)^2}{\pi\left(\frac{15.2\text{ mm}}{2}\right)^2}\right] \times 100 = 43.8\%\text{CW}$$

For the rectangular one

$$\%\text{CW} = \left[\frac{(125\text{ mm})(175\text{ mm}) - (75\text{ mm})(200\text{ mm})}{(125\text{ mm})(175\text{ mm})}\right] \times 100 = 31.4\%\text{CW}$$

Therefore, the deformed circular specimen will be harder.

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7.30 *A cylindrical specimen of cold-worked copper has a ductility (%EL) of 25%. If its cold-worked radius is 10 mm (0.40 in.), what was its radius before deformation?*

Solution

This problem calls for us to calculate the precold-worked radius of a cylindrical specimen of copper that has a cold-worked ductility of 25%EL. From Figure 7.19*c*, copper that has a ductility of 25%EL will have experienced a deformation of about 11%CW. For a cylindrical specimen, Equation 7.8 becomes

$$\%\text{CW} = \left[\frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2} \right] \times 100$$

Since $r_d = 10$ mm (0.40 in.), solving for r_0 yields

$$r_0 = \frac{r_d}{\sqrt{1 - \frac{\%\text{CW}}{100}}} = \frac{10 \text{ mm}}{\sqrt{1 - \frac{11.0}{100}}} = 10.6 \text{ mm} \quad (0.424 \text{ in.})$$

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7.31 *(a) What is the approximate ductility (%EL) of a brass that has a yield strength of 275 MPa (40,000 psi)?*

(b) What is the approximate Brinell hardness of a 1040 steel having a yield strength of 690 MPa (100,000 psi)?

Solution

(a) In order to solve this problem, it is necessary to consult Figures 7.19*a* and 7.19*c*. From Figure 7.19*a*, a yield strength of 275 MPa for brass corresponds to 10%CW. A brass that has been cold-worked 10% will have a ductility of about 43%EL [Figure 7.19*c*].

(b) This portion of the problem asks for the Brinell hardness of a 1040 steel having a yield strength of 690 MPa (100,000 psi). From Figure 7.19*a*, a yield strength of 690 MPa for a 1040 steel corresponds to about 10%CW. A 1040 steel that has been cold worked 10% will have a tensile strength of about 780 MPa [Figure 7.19*b*]. Finally, using Equation 6.20a

$$\text{HB} = \frac{TS(\text{MPa})}{3.45} = \frac{780\ \text{MPa}}{3.45} = 226$$

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7.32 *Experimentally, it has been observed for single crystals of a number of metals that the critical resolved shear stress τ_{crss} is a function of the dislocation density ρ_D as*

$$\tau_{crss} = \tau_0 + A\sqrt{\rho_D}$$

where τ_0 and A are constants. For copper, the critical resolved shear stress is 2.10 MPa (305 psi) at a dislocation density of 10^5 mm^{-2}. If it is known that the value of A for copper is 6.35×10^{-3} MPa-mm (0.92 psi-mm), compute the τ_{crss} at a dislocation density of 10^7 mm^{-2}.

Solution

We are asked in this problem to compute the critical resolved shear stress at a dislocation density of 10^7 mm^{-2}. It is first necessary to compute the value of the constant τ_0 (in the equation provided in the problem statement) from the one set of data as

$$\tau_0 = \tau_{crss} - A\sqrt{\rho_D}$$

$$= 2.10 \text{ MPa} - \left(6.35 \times 10^{-3} \text{ MPa - mm}\right)\left(\sqrt{10^5 \text{ mm}^{-2}}\right) = 0.092 \text{ MPa} \quad (13.3 \text{ psi})$$

Now, the critical resolved shear stress may be determined at a dislocation density of 10^7 mm^{-2} as

$$\tau_{crss} = \tau_0 + A\sqrt{\rho_D}$$

$$= (0.092 \text{ MPa}) + \left(6.35 \times 10^{-3} \text{ MPa - mm}\right)\sqrt{10^7 \text{ mm}^{-2}} = 20.2 \text{ MPa} \quad (2920 \text{ psi})$$

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Recovery
Recrystallization
Grain Growth

7.33 *Briefly cite the differences between recovery and recrystallization processes.*

Solution

For recovery, there is some relief of internal strain energy by dislocation motion; however, there are virtually no changes in either the grain structure or mechanical characteristics. During recrystallization, on the other hand, a new set of strain-free grains forms, and the material becomes softer and more ductile.

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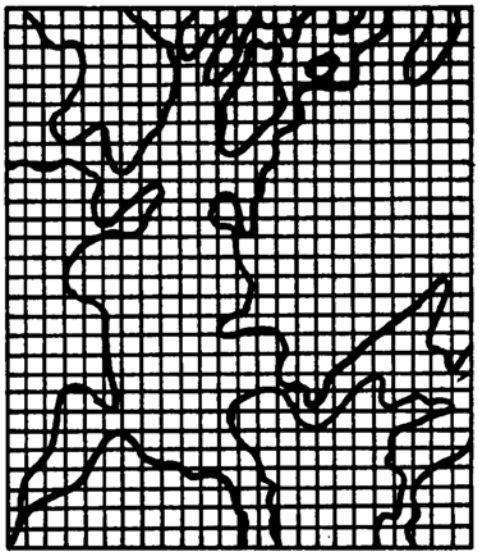
7.34 *Estimate the fraction of recrystallization from the photomicrograph in Figure 7.21c.*

Solution

Below is shown a square grid onto which is superimposed the recrystallized regions from the micrograph. Approximately 400 squares lie within the recrystallized areas, and since there are 672 total squares, the specimen is about 60% recrystallized.



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7.35 *Explain the differences in grain structure for a metal that has been cold worked and one that has been cold worked and then recrystallized.*

Solution

During cold-working, the grain structure of the metal has been distorted to accommodate the deformation. Recrystallization produces grains that are equiaxed and smaller than the parent grains.

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7.36 *(a) What is the driving force for recrystallization?*

(b) For grain growth?

Solution

(a) The driving force for recrystallization is the difference in internal energy between the strained and unstrained material.

(b) The driving force for grain growth is the reduction in grain boundary energy as the total grain boundary area decreases.

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7.37 *(a) From Figure 7.25, compute the length of time required for the average grain diameter to increase from 0.01 to 0.1 mm at 500°C for this brass material.*

(b) Repeat the calculation at 600°C.

Solution

(a) At 500°C, the time necessary for the average grain diameter to grow to increase from 0.01 to 0.1 mm is approximately 3500 min.

(b) At 600°C the time required for this same grain size increase is approximately 150 min.

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7.38 *The average grain diameter for a brass material was measured as a function of time at 650°C, which is tabulated below at two different times:*

Time (min)	***Grain Diameter (mm)***
30	3.9×10^{-2}
90	6.6×10^{-2}

(a) What was the original grain diameter?

(b) What grain diameter would you predict after 150 min at 650°C?

Solution

(a) Using the data given and Equation 7.9 (taking $n = 2$), we may set up two simultaneous equations with d_0 and K as unknowns; thus

$$(3.9 \times 10^{-2}\ \text{mm})^2 - d_0^2 = (30\ \text{min})K$$

$$(6.6 \times 10^{-2}\ \text{mm})^2 - d_0^2 = (90\ \text{min})K$$

Solution of these expressions yields a value for d_0, the original grain diameter, of

$$d_0 = 0.01\ \text{mm},$$

and a value for K of $4.73 \times 10^{-5}\ \text{mm}^2/\text{min}$

(b) At 150 min, the diameter d is computed using a rearranged form of Equation 7.9 as

$$d = \sqrt{d_0^2 + Kt}$$

$$= \sqrt{(0.01\ \text{mm})^2 + (4.73 \times 10^{-5}\ \text{mm}^2/\text{min})(150\ \text{min})} = 0.085\ \text{mm}$$

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7.39 *An undeformed specimen of some alloy has an average grain diameter of 0.040 mm. You are asked to reduce its average grain diameter to 0.010 mm. Is this possible? If so, explain the procedures you would use and name the processes involved. If it is not possible, explain why.*

Solution

Yes, it is possible to reduce the average grain diameter of an undeformed alloy specimen from 0.040 mm to 0.010 mm. In order to do this, plastically deform the material at room temperature (i.e., cold work it), and then anneal at an elevated temperature in order to allow recrystallization and some grain growth to occur until the average grain diameter is 0.010 mm.

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7.40 *Grain growth is strongly dependent on temperature (i.e., rate of grain growth increases with increasing temperature), yet temperature is not explicitly given as a part of Equation 7.9.*

(a) Into which of the parameters in this expression would you expect temperature to be included?

(b) On the basis of your intuition, cite an explicit expression for this temperature dependence.

Solution

(a) The temperature dependence of grain growth is incorporated into the constant K in Equation 7.9.

(b) The explicit expression for this temperature dependence is of the form

$$K = K_0 \exp\left(-\frac{Q}{RT}\right)$$

in which K_0 is a temperature-independent constant, the parameter Q is an activation energy, and R and T are the gas constant and absolute temperature, respectively.

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7.41 *An uncold-worked brass specimen of average grain size 0.008 mm has a yield strength of 160 MPa (23,500 psi). Estimate the yield strength of this alloy after it has been heated to 600°C for 1000 s, if it is known that the value of k_y is 12.0 MPa-mm$^{1/2}$ (1740 psi-mm$^{1/2}$).*

Solution

In order to solve this problem, it is first necessary to calculate the constant σ_0 in Equation 7.7 as

$$\sigma_0 = \sigma_y - k_y d^{-1/2}$$

$$= 160\ \text{MPa} - (12.0\ \text{MPa} - \text{mm}^{1/2})(0.008\ \text{mm})^{-1/2} = 25.8\ \text{MPa}\ (4046\ \text{psi})$$

Next, we must determine the average grain size after the heat treatment. From Figure 7.25 at 600°C after 1000 s (16.7 min) the average grain size of a brass material is about 0.20 mm. Therefore, calculating σ_y at this new grain size using Equation 7.7 we get

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$

$$= 25.8\ \text{MPa} + (12.0\ \text{MPa} - \text{mm}^{1/2})(0.20\ \text{mm})^{-1/2} = 52.6\ \text{MPa}\ (7940\ \text{psi})$$

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DESIGN PROBLEMS

Strain Hardening
Recrystallization

7.D1 *Determine whether or not it is possible to cold work steel so as to give a minimum Brinell hardness of 225, and at the same time have a ductility of at least 12%EL. Justify your decision.*

Solution

The tensile strength corresponding to a Brinell hardness of 225 may be determined using Equation 6.20a as

$$TS(\text{MPa}) = 3.45 \times \text{HB} = (3.45)(225) = 776 \text{ MPa}$$

Furthermore, from Figure 7.19*b*, in order to achieve a tensile strength of 776 MPa, deformation of at least 9%CW is necessary. Finally, if we cold work the steel to 9%CW, then the ductility is 17%EL from Figure 7.19*c*. Therefore, it *is possible* to meet both of these criteria by plastically deforming the steel.

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7.D2 *Determine whether or not it is possible to cold work brass so as to give a minimum Brinell hardness of 120 and at the same time have a ductility of at least 20%EL. Justify your decision.*

Solution

According to Figure 6.19, a Brinell hardness of 120 corresponds to a tensile strength of 440 MPa (63,500 psi.) Furthermore, from Figure 7.19*b*, in order to achieve a tensile strength of 440 MPa, deformation of at least 26%CW is necessary. Finally, if we are to achieve a ductility of at least 20%EL, then a maximum deformation of 23%CW is possible from Figure 7.19*c*. Therefore, it is *not possible* to meet both of these criteria by plastically deforming brass.

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7.D3 *A cylindrical specimen of cold-worked steel has a Brinell hardness of 250.*

(a) Estimate its ductility in percent elongation.

(b) If the specimen remained cylindrical during deformation and its original radius was 5 mm (0.20 in.), determine its radius after deformation.

Solution

(a) From Figure 6.19, a Brinell hardness of 250 corresponds to a tensile strength of 860 MPa (125,000 psi), which, from Figure 7.19*b*, requires a deformation of 25%CW. Furthermore, 25%CW yields a ductility of about 11%EL for steel, Figure 7.19*c*.

(b) We are now asked to determine the radius after deformation if the uncold-worked radius is 5 mm (0.20 in.). From Equation 7.8 and for a cylindrical specimen

$$\%\text{CW} = \left[\frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2} \right] \times 100$$

Now, solving for r_d from this expression, we get

$$r_d = r_0 \sqrt{1 - \frac{\%\text{CW}}{100}}$$

$$= (5 \text{ mm}) \sqrt{1 - \frac{25}{100}} = 4.33 \text{ mm} \quad (0.173 \text{ in.})$$

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7.D4 *It is necessary to select a metal alloy for an application that requires a yield strength of at least 345 MPa (50,000 psi) while maintaining a minimum ductility (%EL) of 20%. If the metal may be cold worked, decide which of the following are candidates: copper, brass, and a 1040 steel. Why?*

Solution

For each of these alloys, the minimum cold work necessary to achieve the yield strength may be determined from Figure 7.19*a*, while the maximum possible cold work for the ductility is found in Figure 7.19*c*. These data are tabulated below.

	Yield Strength (> 345 MPa)	Ductility (> 20%EL)
Steel	Any %CW	< 5%CW
Brass	> 20%CW	< 23%CW
Copper	> 54%CW	< 15%CW

Thus, both the 1040 steel and brass are possible candidates since for these alloys there is an overlap of percents coldwork to give the required minimum yield strength and ductility values.

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7.D5 *A cylindrical rod of 1040 steel originally 15.2 mm (0.60 in.) in diameter is to be cold worked by drawing; the circular cross section will be maintained during deformation. A cold-worked tensile strength in excess of 840 MPa (122,000 psi) and a ductility of at least 12%EL are desired. Furthermore, the final diameter must be 10 mm (0.40 in.). Explain how this may be accomplished.*

Solution

First let us calculate the percent cold work and attendant tensile strength and ductility if the drawing is carried out without interruption. From Equation 7.8

$$\%\text{CW} = \frac{\pi\left(\frac{d_0}{2}\right)^2 - \pi\left(\frac{d_d}{2}\right)^2}{\pi\left(\frac{d_0}{2}\right)^2} \times 100$$

$$= \frac{\pi\left(\frac{15.2\ \text{mm}}{2}\right)^2 - \pi\left(\frac{10\ \text{mm}}{2}\right)^2}{\pi\left(\frac{15.2\ \text{mm}}{2}\right)^2} \times 100 = 56\%\text{CW}$$

At 56%CW, the steel will have a tensile strength on the order of 920 MPa (133,000 psi) [Figure 7.19*b*], which is adequate; however, the ductility will be less than 10%EL [Figure 7.19*c*], which is insufficient.

Instead of performing the drawing in a single operation, let us initially draw some fraction of the total deformation, then anneal to recrystallize, and, finally, cold-work the material a second time in order to achieve the final diameter, tensile strength, and ductility.

Reference to Figure 7.19*b* indicates that 20%CW is necessary to yield a tensile strength of 840 MPa (122,000 psi). Similarly, a maximum of 21%CW is possible for 12%EL [Figure 7.19*c*]. The average of these extremes is 20.5%CW. Again using Equation 7.8, if the final diameter after the first drawing is d_0', then

$$20.5\%\text{CW} = \frac{\pi\left(\frac{d_0'}{2}\right)^2 - \pi\left(\frac{10\ \text{mm}}{2}\right)^2}{\pi\left(\frac{d_0'}{2}\right)^2} \times 100$$

And, solving the above expression for d_0', yields

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$$d_0' = \frac{10 \text{ mm}}{\sqrt{1 - \frac{20.5\%\text{CW}}{100}}} = 11.2 \text{ mm } (0.45 \text{ in.})$$

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7.D6 *A cylindrical rod of copper originally 16.0 mm (0.625 in.) in diameter is to be cold worked by drawing; the circular cross section will be maintained during deformation. A cold-worked yield strength in excess of 250 MPa (36,250 psi) and a ductility of at least 12%EL are desired. Furthermore, the final diameter must be 11.3 mm (0.445 in.). Explain how this may be accomplished.*

Solution

Let us first calculate the percent cold work and attendant yield strength and ductility if the drawing is carried out without interruption. From Equation 7.8

$$\%\text{CW} = \frac{\pi\left(\frac{d_0}{2}\right)^2 - \pi\left(\frac{d_d}{2}\right)^2}{\pi\left(\frac{d_0}{2}\right)^2} \times 100$$

$$= \frac{\pi\left(\frac{16.0\ \text{mm}}{2}\right)^2 - \pi\left(\frac{11.3\ \text{mm}}{2}\right)^2}{\pi\left(\frac{16.0\ \text{mm}}{2}\right)^2} \times 100 = 50\%\text{CW}$$

At 50%CW, the copper will have a yield strength on the order of 330 MPa (48,000 psi), Figure 7.19*a*, which is adequate; however, the ductility will be about 4%EL, Figure 7.19*c*, which is insufficient.

Instead of performing the drawing in a single operation, let us initially draw some fraction of the total deformation, then anneal to recrystallize, and, finally, cold work the material a second time in order to achieve the final diameter, yield strength, and ductility.

Reference to Figure 7.19*a* indicates that 21%CW is necessary to give a yield strength of 250 MPa. Similarly, a maximum of 23%CW is possible for 12%EL [Figure 7.19*c*]. The average of these two values is 22%CW, which we will use in the calculations. Thus, to achieve both the specified yield strength and ductility, the copper must be deformed to 22%CW. If the final diameter after the first drawing is d_0', then, using Equation 7.8

$$22\%\text{CW} = \frac{\pi\left(\frac{d_0'}{2}\right)^2 - \pi\left(\frac{11.3\ \text{mm}}{2}\right)^2}{\pi\left(\frac{d_0'}{2}\right)^2} \times 100$$

And, solving for d_0' from the above expression yields

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$$d_0' = \frac{11.3 \text{ mm}}{\sqrt{1 - \frac{22\%\text{CW}}{100}}} = 12.8 \text{ mm } (0.50 \text{ in.})$$

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7.D7 *A cylindrical 1040 steel rod having a minimum tensile strength of 865 MPa (125,000 psi), a ductility of at least 10%EL, and a final diameter of 6.0 mm (0.25 in.) is desired. Some 7.94 mm (0.313 in.) diameter 1040 steel stock, which has been cold worked 20% is available. Describe the procedure you would follow to obtain this material. Assume that 1040 steel experiences cracking at 40%CW.*

Solution

This problem calls for us to cold work some 1040 steel stock that has been previously cold worked in order to achieve minimum tensile strength and ductility values of 865 MPa (125,000 psi) and 10%EL, respectively, while the final diameter must be 6.0 mm (0.25 in.). Furthermore, the material may not be deformed beyond 40%CW. Let us start by deciding what percent coldwork is necessary for the minimum tensile strength and ductility values, assuming that a recrystallization heat treatment is possible. From Figure 7.19*b*, at least 25%CW is required for a tensile strength of 865 MPa. Furthermore, according to Figure 7.19*c*, 10%EL corresponds a maximum of 30%CW. Let us take the average of these two values (i.e., 27.5%CW), and determine what previous specimen diameter is required to yield a final diameter of 6.0 mm. For cylindrical specimens, Equation 7.8 takes the form

$$\%CW = \frac{\pi\left(\frac{d_0}{2}\right)^2 - \pi\left(\frac{d_d}{2}\right)^2}{\pi\left(\frac{d_0}{2}\right)^2} \times 100$$

Solving for the original diameter d_0 yields

$$d_0 = \frac{d_d}{\sqrt{1 - \frac{\%CW}{100}}} = \frac{6.0 \text{ mm}}{\sqrt{1 - \frac{27.5\%CW}{100}}} = 7.05 \text{ mm} \quad (0.278 \text{ in.})$$

Now, let us determine its undeformed diameter realizing that a diameter of 7.94 mm corresponds to 20%CW. Again solving for d_0 using the above equation and assuming $d_d = 7.94$ mm yields

$$d_0 = \frac{d_d}{\sqrt{1 - \frac{\%CW}{100}}} = \frac{7.94 \text{ mm}}{\sqrt{1 - \frac{20\%CW}{100}}} = 8.88 \text{ mm} \quad (0.350 \text{ in.})$$

At this point let us see if it is possible to deform the material from 8.88 mm to 7.05 mm without exceeding the 40%CW limit. Again employing Equation 7.8

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$$\%CW = \frac{\pi\left(\frac{8.88\ \text{mm}}{2}\right)^2 - \pi\left(\frac{7.05\ \text{mm}}{2}\right)^2}{\pi\left(\frac{8.88\ \text{mm}}{2}\right)^2} \times 100 = 37\%CW$$

In summary, the procedure which can be used to produce the desired material would be as follows: cold work the as-received stock to 7.05 mm (0.278 in.), heat treat it to achieve complete recrystallization, and then cold work the material again to 6.0 mm (0.25 in.), which will give the desired tensile strength and ductility.

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CHAPTER 8

FAILURE

PROBLEM SOLUTIONS

Principles of Fracture Mechanics

8.1 *What is the magnitude of the maximum stress that exists at the tip of an internal crack having a radius of curvature of 2.5 × 10^{-4} mm (10^{-5} in.) and a crack length of 2.5 × 10^{-2} mm (10^{-3} in.) when a tensile stress of 170 MPa (25,000 psi) is applied?*

Solution

This problem asks that we compute the magnitude of the maximum stress that exists at the tip of an internal crack. Equation 8.1 is employed to solve this problem, as

$$\sigma_m = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2}$$

$$= (2)(170\ \text{MPa})\left[\frac{\frac{2.5 \times 10^{-2}\ \text{mm}}{2}}{2.5 \times 10^{-4}\ \text{mm}}\right]^{1/2} = 2404\ \text{MPa}\quad (354{,}000\ \text{psi})$$

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8.2 *Estimate the theoretical fracture strength of a brittle material if it is known that fracture occurs by the propagation of an elliptically shaped surface crack of length 0.25 mm (0.01 in.) and having a tip radius of curvature of 1.2×10^{-3} mm (4.7×10^{-5} in.) when a stress of 1200 MPa (174,000 psi) is applied.*

Solution

In order to estimate the theoretical fracture strength of this material it is necessary to calculate σ_m using Equation 8.1 given that $\sigma_0 = 1200$ MPa, $a = 0.25$ mm, and $\rho_t = 1.2 \times 10^{-3}$ mm. Thus,

$$\sigma_m = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2}$$

$$= (2)(1200\ \text{MPa})\left[\frac{0.25\ \text{mm}}{1.2 \times 10^{-3}\ \text{mm}}\right]^{1/2} = 3.5 \times 10^4\ \text{MPa} = 35\ \text{GPa}\ \ (5.1 \times 10^6\ \text{psi})$$

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8.3 *If the specific surface energy for soda-lime glass is 0.30 J/m^2, using data contained in Table 12.5, compute the critical stress required for the propagation of a surface crack of length 0.05 mm.*

Solution

We may determine the critical stress required for the propagation of an surface crack in soda-lime glass using Equation 8.3; taking the value of 69 GPa (Table 12.5) as the modulus of elasticity, we get

$$\sigma_c = \left[\frac{2E\gamma_s}{\pi a}\right]^{1/2}$$

$$= \left[\frac{(2)\left(69 \times 10^9 \text{ N/m}^2\right)(0.30 \text{ N/m})}{(\pi)\left(0.05 \times 10^{-3} \text{ m}\right)}\right]^{1/2} = 16.2 \times 10^6 \text{ N/m}^2 = 16.2 \text{ MPa}$$

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8.4 *A polystyrene component must not fail when a tensile stress of 1.25 MPa (180 psi) is applied. Determine the maximum allowable surface crack length if the surface energy of polystyrene is 0.50 J/m^2 (2.86 $\times$ 10^{-3} in.-lb$_f$/in.^{2}). Assume a modulus of elasticity of 3.0 GPa (0.435 $\times$ 10^6 psi).*

Solution

The maximum allowable surface crack length for polystyrene may be determined using Equation 8.3; taking 3.0 GPa as the modulus of elasticity, and solving for a, leads to

$$a = \frac{2E\gamma_s}{\pi\sigma_c^2} = \frac{(2)\left(3 \times 10^9 \text{ N/m}^2\right)(0.50 \text{ N/m})}{(\pi)\left(1.25 \times 10^6 \text{ N/m}^2\right)^2}$$

$$= 6.1 \times 10^{-4} \text{ m} = 0.61 \text{ mm} \quad (0.024 \text{ in.})$$

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8.5 *A specimen of a 4340 steel alloy having a plane strain fracture toughness of 45 MPa$\sqrt{m}$ (41 ksi$\sqrt{in.}$) is exposed to a stress of 1000 MPa (145,000 psi). Will this specimen experience fracture if it is known that the largest surface crack is 0.75 mm (0.03 in.) long? Why or why not? Assume that the parameter Y has a value of 1.0.*

Solution

This problem asks us to determine whether or not the 4340 steel alloy specimen will fracture when exposed to a stress of 1000 MPa, given the values of K_{Ic}, Y, and the largest value of a in the material. This requires that we solve for σ_c from Equation 8.6. Thus

$$\sigma_c = \frac{K_{Ic}}{Y\sqrt{\pi a}} = \frac{45\ \text{MPa}\sqrt{\text{m}}}{(1.0)\sqrt{(\pi)(0.75 \times 10^{-3}\ \text{m})}} = 927\ \text{MPa} \quad (133,500\ \text{psi})$$

Therefore, fracture will most likely occur because this specimen will tolerate a stress of 927 MPa (133,500 psi) before fracture, which is less than the applied stress of 1000 MPa (145,000 psi).

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8.6 *Some aircraft component is fabricated from an aluminum alloy that has a plane strain fracture toughness of 35 MPa$\sqrt{m}$ (31.9 ksi$\sqrt{in.}$). It has been determined that fracture results at a stress of 250 MPa (36,250 psi) when the maximum (or critical) internal crack length is 2.0 mm (0.08 in.). For this same component and alloy, will fracture occur at a stress level of 325 MPa (47,125 psi) when the maximum internal crack length is 1.0 mm (0.04 in.)? Why or why not?*

Solution

We are asked to determine if an aircraft component will fracture for a given fracture toughness (35 MPa$\sqrt{\text{m}}$), stress level (325 MPa), and maximum internal crack length (1.0 mm), given that fracture occurs for the same component using the same alloy for another stress level and internal crack length. It first becomes necessary to solve for the parameter Y, using Equation 8.5, for the conditions under which fracture occurred (i.e., σ = 250 MPa and $2a$ = 2.0 mm). Therefore,

$$Y = \frac{K_{Ic}}{\sigma\sqrt{\pi a}} = \frac{35\ \text{MPa}\sqrt{\text{m}}}{(250\ \text{MPa})\sqrt{(\pi)\left(\frac{2 \times 10^{-3}\ \text{m}}{2}\right)}} = 2.50$$

Now we will solve for the product $Y\sigma\sqrt{\pi a}$ for the other set of conditions, so as to ascertain whether or not this value is greater than the K_{Ic} for the alloy. Thus,

$$Y\sigma\sqrt{\pi a} = (2.50)(325\ \text{MPa})\sqrt{(\pi)\left(\frac{1 \times 10^{-3}\ \text{m}}{2}\right)}$$

$$= 32.2\ \text{MPa}\sqrt{\text{m}} \quad (29.5\ \text{ksi}\sqrt{\text{in.}})$$

Therefore, fracture *will not* occur since this value (32.3 MPa$\sqrt{\text{m}}$) is less than the K_{Ic} of the material, 35 MPa$\sqrt{\text{m}}$.

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8.7 *Suppose that a wing component on an aircraft is fabricated from an aluminum alloy that has a plane strain fracture toughness of 40 MPa$\sqrt{m}$ (36.4 ksi$\sqrt{in.}$). It has been determined that fracture results at a stress of 365 MPa (53,000 psi) when the maximum internal crack length is 2.5 mm (0.10 in.). For this same component and alloy, compute the stress level at which fracture will occur for a critical internal crack length of 4.0 mm (0.16 in.).*

Solution

This problem asks us to determine the stress level at which an a wing component on an aircraft will fracture for a given fracture toughness $\left(40\ \text{MPa}\sqrt{\text{m}}\right)$ and maximum internal crack length (4.0 mm), given that fracture occurs for the same component using the same alloy at one stress level (365 MPa) and another internal crack length (2.5 mm). It first becomes necessary to solve for the parameter Y for the conditions under which fracture occurred using Equation 8.5. Therefore,

$$Y = \frac{K_{Ic}}{\sigma\sqrt{\pi a}} = \frac{40\ \text{MPa}\sqrt{\text{m}}}{(365\ \text{MPa})\sqrt{(\pi)\left(\frac{2.5 \times 10^{-3}\ \text{m}}{2}\right)}} = 1.75$$

Now we will solve for σ_c using Equation 8.6 as

$$\sigma_c = \frac{K_{Ic}}{Y\sqrt{\pi a}} = \frac{40\ \text{MPa}\sqrt{\text{m}}}{(1.75)\sqrt{(\pi)\left(\frac{4 \times 10^{-3}\ \text{m}}{2}\right)}} = 288\ \text{MPa}\quad (41{,}500\ \text{psi})$$

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8.8 *A large plate is fabricated from a steel alloy that has a plane strain fracture toughness of 55 MPa$\sqrt{m}$ (50 ksi$\sqrt{in.}$). If, during service use, the plate is exposed to a tensile stress of 200 MPa (29,000 psi), determine the minimum length of a surface crack that will lead to fracture. Assume a value of 1.0 for Y.*

Solution

For this problem, we are given values of K_{Ic} (55 MPa$\sqrt{\text{m}}$), σ (200 MPa), and Y (1.0) for a large plate and are asked to determine the minimum length of a surface crack that will lead to fracture. All we need do is to solve for a_c using Equation 8.7; therefore

$$a_c = \frac{1}{\pi}\left(\frac{K_{Ic}}{Y\sigma}\right)^2 = \frac{1}{\pi}\left[\frac{55\ \text{MPa}\sqrt{\text{m}}}{(1.0)(200\ \text{MPa})}\right]^2 = 0.024\ \text{m} = 24\ \text{mm}\quad (0.95\ \text{in.})$$

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8.9 *Calculate the maximum internal crack length allowable for a 7075-T651 aluminum alloy (Table 8.1) component that is loaded to a stress one half of its yield strength. Assume that the value of Y is 1.35.*

Solution

This problem asks us to calculate the maximum internal crack length allowable for the 7075-T651 aluminum alloy in Table 8.1 given that it is loaded to a stress level equal to one-half of its yield strength. For this alloy, $K_{Ic} = 24\ \text{MPa}\sqrt{\text{m}}\ \ (22\ \text{ksi}\sqrt{\text{in.}})$; also, $\sigma = \sigma_y/2 = (495\ \text{MPa})/2 = 248\ \text{MPa}$ (36,000 psi). Now solving for $2a_c$ using Equation 8.7 yields

$$2a_c = \frac{2}{\pi}\left(\frac{K_{Ic}}{Y\sigma}\right)^2 = \frac{2}{\pi}\left[\frac{24\ \text{MPa}\sqrt{\text{m}}}{(1.35)(248\ \text{MPa})}\right]^2 = 0.0033\ \text{m} = 3.3\ \text{mm}\quad (0.13\ \text{in.})$$

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8.10 *A structural component in the form of a wide plate is to be fabricated from a steel alloy that has a plane strain fracture toughness of 77.0 MPa$\sqrt{m}$ (70.1 ksi$\sqrt{in.}$) and a yield strength of 1400 MPa (205,000 psi). The flaw size resolution limit of the flaw detection apparatus is 4.0 mm (0.16 in.). If the design stress is one half of the yield strength and the value of Y is 1.0, determine whether or not a critical flaw for this plate is subject to detection.*

Solution

This problem asks that we determine whether or not a critical flaw in a wide plate is subject to detection given the limit of the flaw detection apparatus (4.0 mm), the value of K_{Ic} $\left(77\ \text{MPa}\sqrt{\text{m}}\right)$, the design stress ($\sigma_y/2$ in which σ_y = 1400 MPa), and Y = 1.0. We first need to compute the value of a_c using Equation 8.7; thus

$$a_c = \frac{1}{\pi}\left(\frac{K_{Ic}}{Y\sigma}\right)^2 = \frac{1}{\pi}\left[\frac{77\ \text{MPa}\sqrt{\text{m}}}{(1.0)\left(\frac{1400\ \text{MPa}}{2}\right)}\right]^2 = 0.0039\ \text{m} = 3.9\ \text{mm}\quad (0.15\ \text{in.})$$

Therefore, the critical flaw is *not* subject to detection since this value of a_c (3.9 mm) is less than the 4.0 mm resolution limit.

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8.11 *After consultation of other references, write a brief report on one or two nondestructive test techniques that are used to detect and measure internal and/or surface flaws in metal alloys.*

The student should do this problem on his/her own.

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Impact Fracture Testing

8.12 *Following is tabulated data that were gathered from a series of Charpy impact tests on a ductile cast iron.*

Temperature (°C)	*Impact Energy (J)*
–25	*124*
–50	*123*
–75	*115*
–85	*100*
–100	*73*
–110	*52*
–125	*26*
–150	*9*
–175	*6*

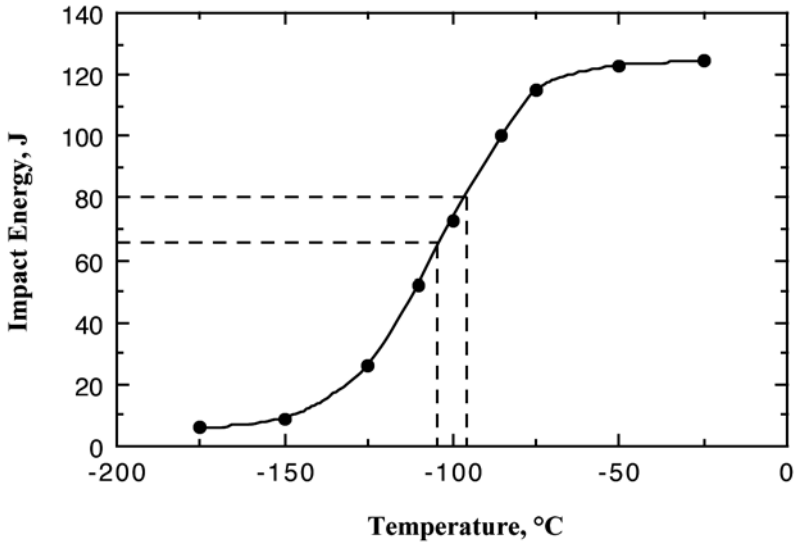
(a) Plot the data as impact energy versus temperature.

(b) Determine a ductile-to-brittle transition temperature as that temperature corresponding to the average of the maximum and minimum impact energies.

(c) Determine a ductile-to-brittle transition temperature as that temperature at which the impact energy is 80 J.

Solution

(a) The plot of impact energy versus temperature is shown below.



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(b) The average of the maximum and minimum impact energies from the data is

$$\text{Average} = \frac{124\ \text{J} + 6\ \text{J}}{2} = 65\ \text{J}$$

As indicated on the plot by the one set of dashed lines, the ductile-to-brittle transition temperature according to this criterion is about –105°C.

(c) Also, as noted on the plot by the other set of dashed lines, the ductile-to-brittle transition temperature for an impact energy of 80 J is about –95°C.

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8.13 *Following is tabulated data that were gathered from a series of Charpy impact tests on a tempered 4140 steel alloy.*

Temperature (°C)	***Impact Energy (J)***
100	*89.3*
75	*88.6*
50	*87.6*
25	*85.4*
0	*82.9*
–25	*78.9*
–50	*73.1*
–65	*66.0*
–75	*59.3*
–85	*47.9*
–100	*34.3*
–125	*29.3*
–150	*27.1*
–175	*25.0*

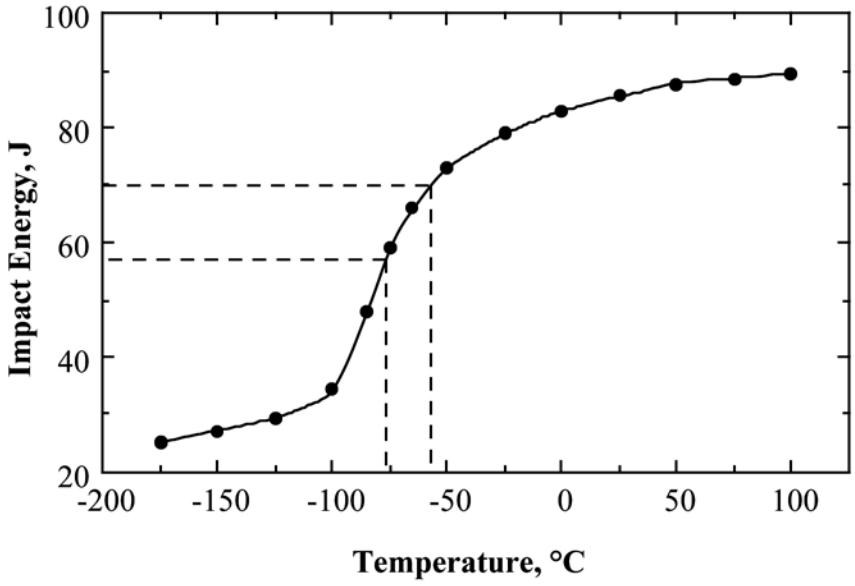
(a) Plot the data as impact energy versus temperature.

(b) Determine a ductile-to-brittle transition temperature as that temperature corresponding to the average of the maximum and minimum impact energies.

(c) Determine a ductile-to-brittle transition temperature as that temperature at which the impact energy is 70 J.

Solution

The plot of impact energy versus temperature is shown below.



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(b) The average of the maximum and minimum impact energies from the data is

$$\text{Average} = \frac{89.3\ \text{J} + 25\ \text{J}}{2} = 57.2\ \text{J}$$

As indicated on the plot by the one set of dashed lines, the ductile-to-brittle transition temperature according to this criterion is about –75°C.

(c) Also, as noted on the plot by the other set of dashed lines, the ductile-to-brittle transition temperature for an impact energy of 70 J is about –55°C.

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Cyclic Stresses (Fatigue)
The *S*-*N* Curve

8.14 *A fatigue test was conducted in which the mean stress was 50 MPa (7250 psi) and the stress amplitude was 225 MPa (32,625 psi).*

(a) Compute the maximum and minimum stress levels.

(b) Compute the stress ratio.

(c) Compute the magnitude of the stress range.

Solution

(a) Given the values of σ_m (50 MPa) and σ_a (225 MPa) we are asked to compute σ_{max} and σ_{min}. From Equation 8.14

$$\sigma_m = \frac{\sigma_{max} + \sigma_{min}}{2} = 50 \text{ MPa}$$

Or,

$$\sigma_{max} + \sigma_{min} = 100 \text{ MPa}$$

Furthermore, utilization of Equation 8.16 yields

$$\sigma_a = \frac{\sigma_{max} - \sigma_{min}}{2} = 225 \text{ MPa}$$

Or,

$$\sigma_{max} - \sigma_{min} = 450 \text{ MPa}$$

Simultaneously solving these two expressions leads to

$$\sigma_{max} = 275 \text{ MPa} \quad (40,000 \text{ psi})$$
$$\sigma_{min} = -175 \text{ MPa} \quad (-25,500 \text{ psi})$$

(b) Using Equation 8.17 the stress ratio R is determined as follows:

$$R = \frac{\sigma_{min}}{\sigma_{max}} = \frac{-175 \text{ MPa}}{275 \text{ MPa}} = -0.64$$

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(c) The magnitude of the stress range σ_r is determined using Equation 8.15 as

$$\sigma_r = \sigma_{max} - \sigma_{min} = 275 \text{ MPa} - (-175 \text{ MPa}) = 450 \text{ MPa} \quad (65,500 \text{ psi})$$

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8.15 *A cylindrical 1045 steel bar (Figure 8.34) is subjected to repeated compression-tension stress cycling along its axis. If the load amplitude is 22,000 N (4950 lb_f), compute the minimum allowable bar diameter to ensure that fatigue failure will not occur. Assume a factor of safety of 2.0.*

Solution

From Figure 8.34, the fatigue limit stress amplitude for this alloy is 310 MPa (45,000 psi). Stress is defined in Equation 6.1 as $\sigma = \frac{F}{A_0}$. For a cylindrical bar

$$A_0 = \pi\left(\frac{d_0}{2}\right)^2$$

Substitution for A_0 into the Equation 6.1 leads to

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{4F}{\pi d_0^2}$$

We now solve for d_0, taking stress as the fatigue limit divided by the factor of safety. Thus

$$d_0 = \sqrt{\frac{4F}{\pi\left(\frac{\sigma}{N}\right)}}$$

$$= \sqrt{\frac{(4)(22{,}000\ \text{N})}{(\pi)\left(\frac{310 \times 10^6\ \text{N/m}^2}{2}\right)}} = 13.4 \times 10^{-3}\ \text{m} = 13.4\ \text{mm}\ \ (0.53\ \text{in.})$$

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8.16 *An 8.0 mm (0.31 in.) diameter cylindrical rod fabricated from a red brass alloy (Figure 8.34) is subjected to reversed tension-compression load cycling along its axis. If the maximum tensile and compressive loads are +7500 N (1700 lb_f) and -7500 N (-1700 lb_f), respectively, determine its fatigue life. Assume that the stress plotted in Figure 8.34 is stress amplitude.*

Solution

We are asked to determine the fatigue life for a cylindrical red brass rod given its diameter (8.0 mm) and the maximum tensile and compressive loads (+7500 N and -7500 N, respectively). The first thing that is necessary is to calculate values of σ_{max} and σ_{min} using Equation 6.1. Thus

$$\sigma_{max} = \frac{F_{max}}{A_0} = \frac{F_{max}}{\pi\left(\frac{d_0}{2}\right)^2}$$

$$= \frac{7500\ \text{N}}{(\pi)\left(\frac{8.0 \times 10^{-3}\ \text{m}}{2}\right)^2} = 150 \times 10^6\ \text{N/m}^2 = 150\ \text{MPa} \quad (22{,}500\ \text{psi})$$

$$\sigma_{min} = \frac{F_{min}}{\pi\left(\frac{d_0}{2}\right)^2}$$

$$= \frac{-7500\ \text{N}}{(\pi)\left(\frac{8.0 \times 10^{-3}\ \text{m}}{2}\right)^2} = -150 \times 10^6\ \text{N/m}^2 = -150\ \text{MPa} \quad (-22{,}500\ \text{psi})$$

Now it becomes necessary to compute the stress amplitude using Equation 8.16 as

$$\sigma_a = \frac{\sigma_{max} - \sigma_{min}}{2} = \frac{150\ \text{MPa} - (-150\ \text{MPa})}{2} = 150\ \text{MPa} \quad (22{,}500\ \text{psi})$$

From Figure 8.34, f for the red brass, the number of cycles to failure at this stress amplitude is about 1×10^5 cycles.

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8.17 *A 12.5 mm (0.50 in.) diameter cylindrical rod fabricated from a 2014-T6 alloy (Figure 8.34) is subjected to a repeated tension-compression load cycling along its axis. Compute the maximum and minimum loads that will be applied to yield a fatigue life of 1.0×10^7 cycles. Assume that the stress plotted on the vertical axis is stress amplitude, and data were taken for a mean stress of 50 MPa (7250 psi).*

Solution

This problem asks that we compute the maximum and minimum loads to which a 12.5 mm (0.50 in.) diameter 2014-T6 aluminum alloy specimen may be subjected in order to yield a fatigue life of 1.0×10^7 cycles; Figure 8.34 is to be used assuming that data were taken for a mean stress of 50 MPa (7250 psi). Upon consultation of Figure 8.34, a fatigue life of 1.0×10^7 cycles corresponds to a stress amplitude of 160 MPa (23,200 psi). Or, from Equation 8.16

$$\sigma_{max} - \sigma_{min} = 2\sigma_a = (2)(160\ \text{MPa}) = 320\ \text{MPa}\ \ (46{,}400\ \text{psi})$$

Since $\sigma_m = 50$ MPa, then from Equation 8.14

$$\sigma_{max} + \sigma_{min} = 2\sigma_m = (2)(50\ \text{MPa}) = 100\ \text{MPa}\ \ (14{,}500\ \text{psi})$$

Simultaneous solution of these two expressions for σ_{max} and σ_{min} yields

$$\sigma_{max} = +210\ \text{MPa}\ \ (+30{,}400\ \text{psi})$$
$$\sigma_{min} = -110\ \text{MPa}\ \ (-16{,}000\ \text{psi})$$

Now, inasmuch as $\sigma = \dfrac{F}{A_0}$ (Equation 6.1), and $A_0 = \pi\left(\dfrac{d_0}{2}\right)^2$ then

$$F_{max} = \frac{\sigma_{max}\pi d_0^2}{4} = \frac{\left(210 \times 10^6\ \text{N/m}^2\right)(\pi)\left(12.5 \times 10^{-3}\ \text{m}\right)^2}{4} = 25{,}800\ \text{N}\ \ (6000\ \text{lb}_\text{f})$$

$$F_{min} = \frac{\sigma_{min}\pi d_0^2}{4} = \frac{\left(-110 \times 10^6\ \text{N/m}^2\right)(\pi)\left(12.5 \times 10^{-3}\ \text{m}\right)^2}{4} = -13{,}500\ \text{N}\ \ (-3140\ \text{lb}_\text{f})$$

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8.18 *The fatigue data for a brass alloy are given as follows:*

Stress Amplitude (MPa)	***Cycles to Failure***
310	2×10^5
223	1×10^6
191	3×10^6
168	1×10^7
153	3×10^7
143	1×10^8
134	3×10^8
127	1×10^9

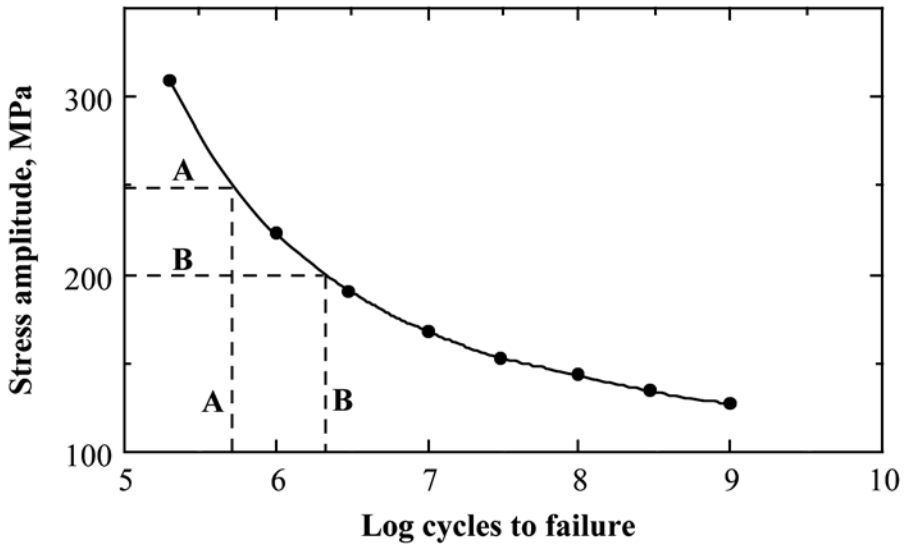
(a) Make an S–N plot (stress amplitude versus logarithm cycles to failure) using these data.

(b) Determine the fatigue strength at 5×10^5 *cycles.*

(c) Determine the fatigue life for 200 MPa.

Solution

(a) The fatigue data for this alloy are plotted below.



(b) As indicated by the "A" set of dashed lines on the plot, the fatigue strength at 5×10^5 cycles [log (5×10^5) = 5.7] is about 250 MPa.

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(c) As noted by the "B" set of dashed lines, the fatigue life for 200 MPa is about 2×10^6 cycles (i.e., the log of the lifetime is about 6.3).

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8.19 *Suppose that the fatigue data for the brass alloy in Problem 8.18 were taken from torsional tests, and that a shaft of this alloy is to be used for a coupling that is attached to an electric motor operating at 1500 rpm. Give the maximum torsional stress amplitude possible for each of the following lifetimes of the coupling: (a) 1 year, (b) 1 month, (c) 1 day, and (d) 2 hours.*

Solution

For each lifetime, first compute the number of cycles, and then read the corresponding fatigue strength from the above plot.

(a) Fatigue lifetime = (1 yr)(365 days/yr)(24 h/day)(60 min/h)(1500 cycles/min) = 7.9×10^8 cycles. The stress amplitude corresponding to this lifetime is about 130 MPa.

(b) Fatigue lifetime = (30 days)(24 h/day)(60 min/h)(1500 cycles/min) = 6.5×10^7 cycles. The stress amplitude corresponding to this lifetime is about 145 MPa.

(c) Fatigue lifetime = (24 h)(60 min/h)(1500 cycles/min) = 2.2×10^6 cycles. The stress amplitude corresponding to this lifetime is about 195 MPa.

(d) Fatigue lifetime = (2 h)(60 min/h)(1500 cycles/min) = 1.8×10^5 cycles. The stress amplitude corresponding to this lifetime is about 315 MPa.

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8.20 *The fatigue data for a ductile cast iron are given as follows:*

***Stress Amplitude* [*MPa* (*ksi*)]**	***Cycles to Failure***
248 (36.0)	1×10^5
236 (34.2)	3×10^5
224 (32.5)	1×10^6
213 (30.9)	3×10^6
201 (29.1)	1×10^7
193 (28.0)	3×10^7
193 (28.0)	1×10^8
193 (28.0)	3×10^8

(a) Make an S–N plot (stress amplitude versus logarithm cycles to failure) using these data.

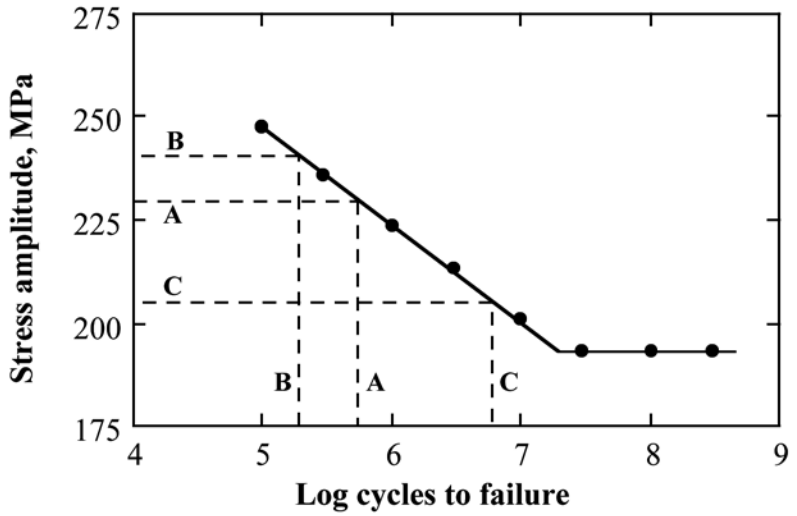
(b) What is the fatigue limit for this alloy?

(c) Determine fatigue lifetimes at stress amplitudes of 230 MPa (33,500 psi) and 175 MPa (25,000 psi).

(d) Estimate fatigue strengths at 2×10^5 and 6×10^6 cycles.

Solution

(a) The fatigue data for this alloy are plotted below.



(b) The fatigue limit is the stress level at which the curve becomes horizontal, which is 193 MPa (28,000 psi).

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(c) As noted by the "A" set of dashed lines, the fatigue lifetime at a stress amplitude of 230 MPa is about 5×10^5 cycles ($\log N = 5.7$). From the plot, the fatigue lifetime at a stress amplitude of 230 MPa (33,500 psi) is about 50,000 cycles ($\log N = 4.7$). At 175 MPa (25,000 psi) the fatigue lifetime is essentially an infinite number of cycles since this stress amplitude is below the fatigue limit.

(d) As noted by the "B" set of dashed lines, the fatigue strength at 2×10^5 cycles ($\log N = 5.3$) is about 240 MPa (35,000 psi); and according to the "C" set of dashed lines, the fatigue strength at 6×10^6 cycles ($\log N = 6.78$) is about 205 MPa (30,000 psi).

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8.21 *Suppose that the fatigue data for the cast iron in Problem 8.20 were taken for bending-rotating tests, and that a rod of this alloy is to be used for an automobile axle that rotates at an average rotational velocity of 750 revolutions per minute. Give maximum lifetimes of continuous driving that are allowable for the following stress levels: (a) 250 MPa (36,250 psi), (b) 215 MPa (31,000 psi), (c) 200 MPa (29,000 psi), and (d) 150 MPa (21,750 psi).*

Solution

For each stress level, first read the corresponding lifetime from the above plot, then convert it into the number of cycles.

(a) For a stress level of 250 MPa (36,250 psi), the fatigue lifetime is approximately 90,000 cycles. This translates into $(9 \times 10^4$ cycles)(1 min/750 cycles) = 120 min.

(b) For a stress level of 215 MPa (31,000 psi), the fatigue lifetime is approximately 2×10^6 cycles. This translates into $(2 \times 10^6$ cycles)(1 min/750 cycles) = 2670 min = 44.4 h.

(c) For a stress level of 200 MPa (29,000 psi), the fatigue lifetime is approximately 1×10^7 cycles. This translates into $(1 \times 10^7$ cycles)(1 min/750 cycles) = 1.33×10^4 min = 222 h.

(d) For a stress level of 150 MPa (21,750 psi), the fatigue lifetime is essentially infinite since we are below the fatigue limit [193 MPa (28,000 psi)].

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8.22 *Three identical fatigue specimens (denoted A, B, and C) are fabricated from a nonferrous alloy. Each is subjected to one of the maximum-minimum stress cycles listed below; the frequency is the same for all three tests.*

Specimen	σ_{max} ***(MPa)***	σ_{min} ***(MPa)***
A	*+450*	*–350*
B	*+400*	*–300*
C	*+340*	*–340*

(a) Rank the fatigue lifetimes of these three specimens from the longest to the shortest.

(b) Now justify this ranking using a schematic S–N plot.

Solution

In order to solve this problem, it is necessary to compute both the mean stress and stress amplitude for each specimen. Since from Equation 8.14, mean stresses are the specimens are determined as follows:

$$\sigma_m = \frac{\sigma_{max} + \sigma_{min}}{2}$$

$$\sigma_m(\text{A}) = \frac{450\ \text{MPa} + (-350\ \text{MPa})}{2} = 50\ \text{MPa}$$

$$\sigma_m(\text{B}) = \frac{400\ \text{MPa} + (-300\ \text{MPa})}{2} = 50\ \text{MPa}$$

$$\sigma_m(\text{C}) = \frac{340\ \text{MPa} + (-340\ \text{MPa})}{2} = 0\ \text{MPa}$$

Furthermore, using Equation 8.16, stress amplitudes are computed as

$$\sigma_a = \frac{\sigma_{max} - \sigma_{min}}{2}$$

$$\sigma_a(\text{A}) = \frac{450\ \text{MPa} - (-350\ \text{MPa})}{2} = 400\ \text{MPa}$$

$$\sigma_a(\text{B}) = \frac{400\ \text{MPa} - (-300\ \text{MPa})}{2} = 350\ \text{MPa}$$

$$\sigma_a(\text{C}) = \frac{340\ \text{MPa} - (-340\ \text{MPa})}{2} = 340\ \text{MPa}$$

On the basis of these results, the fatigue lifetime for specimen C will be greater than specimen B, which in turn will be greater than specimen A. This conclusion is based upon the following *S*-*N* plot on which curves are plotted for two σ_m values.

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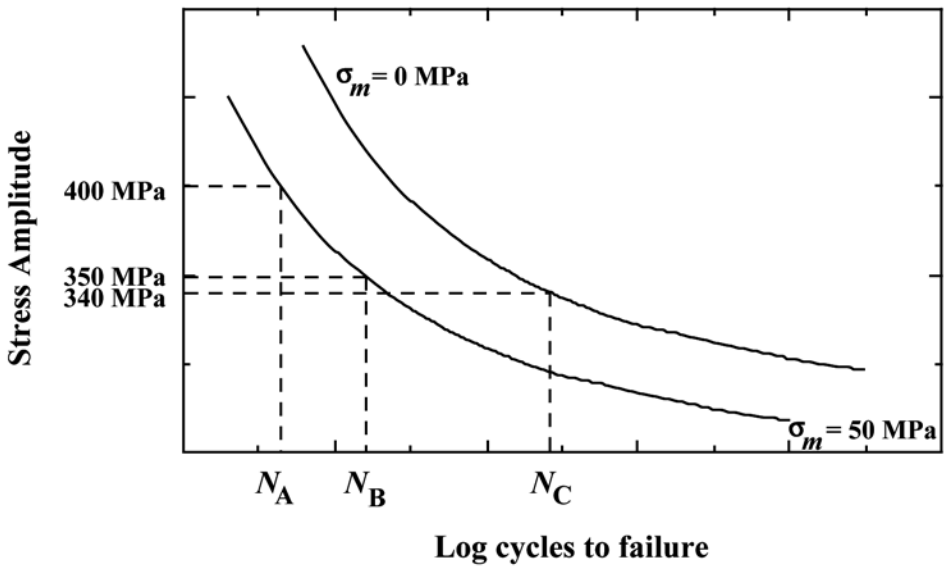

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8.23 *Cite five factors that may lead to scatter in fatigue life data.*

Solution

Five factors that lead to scatter in fatigue life data are (1) specimen fabrication and surface preparation, (2) metallurgical variables, (3) specimen alignment in the test apparatus, (4) variation in mean stress, and (5) variation in test cycle frequency.

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Crack Initiation and Propagation
Factors That Affect Fatigue Life

8.24 *Briefly explain the difference between fatigue striations and beachmarks both in terms of (a) size and (b) origin.*

Solution

(a) With regard to size, beachmarks are normally of macroscopic dimensions and may be observed with the naked eye; fatigue striations are of microscopic size and it is necessary to observe them using electron microscopy.

(b) With regard to origin, beachmarks result from interruptions in the stress cycles; each fatigue striation is corresponds to the advance of a fatigue crack during a single load cycle.

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8.25 *List four measures that may be taken to increase the resistance to fatigue of a metal alloy.*

Solution

Four measures that may be taken to increase the fatigue resistance of a metal alloy are:

(1) Polish the surface to remove stress amplification sites.

(2) Reduce the number of internal defects (pores, etc.) by means of altering processing and fabrication techniques.

(3) Modify the design to eliminate notches and sudden contour changes.

(4) Harden the outer surface of the structure by case hardening (carburizing, nitriding) or shot peening.

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Generalized Creep Behavior

8.26 *Give the approximate temperature at which creep deformation becomes an important consideration for each of the following metals: nickel, copper, iron, tungsten, lead, and aluminum.*

Solution

Creep becomes important at about $0.4T_m$, T_m being the absolute melting temperature of the metal. (The melting temperatures in degrees Celsius are found inside the front cover of the book.)

For Ni, $0.4T_m = (0.4)(1455 + 273) = 691$ K or 418°C (785°F)

For Cu, $0.4T_m = (0.4)(1085 + 273) = 543$ K or 270°C (518°F)

For Fe, $0.4T_m = (0.4)(1538 + 273) = 725$ K or 450°C (845°F)

For W, $0.4T_m = (0.4)(3410 + 273) = 1473$ K or 1200°C (2190°F)

For Pb, $0.4T_m = (0.4)(327 + 273) = 240$ K or –33°C (–27°F)

For Al, $0.4T_m = (0.4)(660 + 273) = 373$ K or 100°C (212°F)

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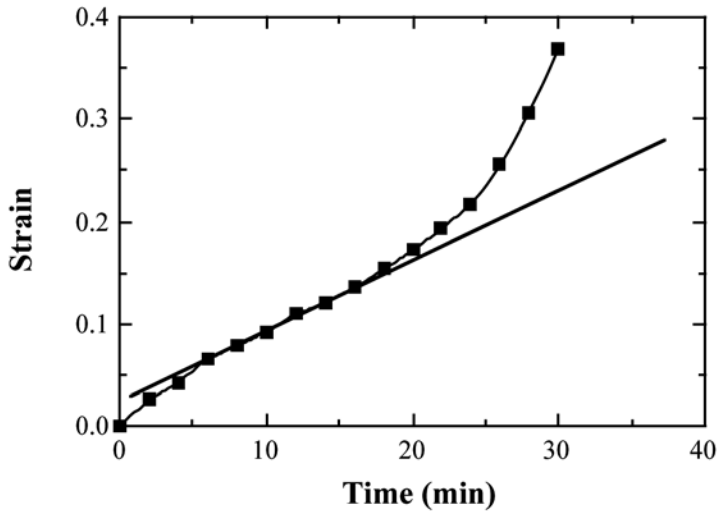
8.27 *The following creep data were taken on an aluminum alloy at 400°C (750°F) and a constant stress of 25 MPa (3660 psi). Plot the data as strain versus time, then determine the steady-state or minimum creep rate. Note: The initial and instantaneous strain is not included.*

***Time* (*min*)**	***Strain***	***Time* (*min*)**	***Strain***
0	*0.000*	*16*	*0.135*
2	*0.025*	*18*	*0.153*
4	*0.043*	*20*	*0.172*
6	*0.065*	*22*	*0.193*
8	*0.078*	*24*	*0.218*
10	*0.092*	*26*	*0.255*
12	*0.109*	*28*	*0.307*
14	*0.120*	*30*	*0.368*

Solution

These creep data are plotted below



The steady-state creep rate ($\Delta\varepsilon/\Delta t$) is the slope of the linear region (i.e., the straight line that has been superimposed on the curve) as

$$\frac{\Delta\varepsilon}{\Delta t} = \frac{0.230 - 0.09}{30\ \text{min} - 10\ \text{min}} = 7.0 \times 10^{-3}\ \text{min}^{-1}$$

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Stress and Temperature Effects

8.28 *A specimen 750 mm (30 in.) long of an S-590 alloy (Figure 8.31) is to be exposed to a tensile stress of 80 MPa (11,600 psi) at 815°C (1500°F). Determine its elongation after 5000 h. Assume that the total of both instantaneous and primary creep elongations is 1.5 mm (0.06 in.).*

Solution

From the 815°C line in Figure 8.31, the steady state creep rate $\dot{\varepsilon}_s$ is about 5.5×10^{-6} h^{-1} at 80 MPa. The steady state creep strain, ε_s, therefore, is just the product of $\dot{\varepsilon}_s$ and time as

$$\varepsilon_s = \dot{\varepsilon}_s \text{ x (time)}$$

$$= \left(5.5 \times 10^{-6}\ h^{-1}\right)(5{,}000\ h) = 0.0275$$

Strain and elongation are related as in Equation 6.2; solving for the steady state elongation, Δl_s, leads to

$$\Delta l_s = l_0 \varepsilon_s = (750\ mm)\left(0.0275\right) = 20.6\ mm \quad (0.81\ in.)$$

Finally, the total elongation is just the sum of this Δl_s and the total of both instantaneous and primary creep elongations [i.e., 1.5 mm (0.06 in.)]. Therefore, the total elongation is 20.6 mm + 1.5 mm = 22.1 mm (0.87 in.).

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8.29 *For a cylindrical S-590 alloy specimen (Figure 8.31) originally 10 mm (0.40 in.) in diameter and 500 mm (20 in.) long, what tensile load is necessary to produce a total elongation of 145 mm (5.7 in.) after 2,000 h at 730°C (1350°F)? Assume that the sum of instantaneous and primary creep elongations is 8.6 mm (0.34 in.).*

Solution

It is first necessary to calculate the steady state creep rate so that we may utilize Figure 8.31 in order to determine the tensile stress. The steady state elongation, Δl_s, is just the difference between the total elongation and the sum of the instantaneous and primary creep elongations; that is,

$$\Delta l_s = 145 \text{ mm} - 8.6 \text{ mm} = 136.4 \text{ mm} \quad (5.36 \text{ in.})$$

Now the steady state creep rate, $\dot{\varepsilon}_s$ is just

$$\dot{\varepsilon}_s = \frac{\Delta \varepsilon}{\Delta t} = \frac{\dfrac{\Delta l_s}{l_0}}{\Delta t} = \frac{\dfrac{136.4 \text{ mm}}{500 \text{ mm}}}{2{,}000 \text{ h}}$$

$$= 1.36 \times 10^{-4} \text{ h}^{-1}$$

Employing the 730°C line in Figure 8.31, a steady state creep rate of 1.36×10^{-4} h^{-1} corresponds to a stress σ of about 200 MPa (or 29,000 psi) [since $\log (1.36 \times 10^{-4}) = -3.866$]. From this we may compute the tensile load using Equation 6.1 as

$$F = \sigma A_0 = \sigma \pi \left(\frac{d_0}{2} \right)^2$$

$$= \left(200 \times 10^6 \text{ N/m}^2\right)(\pi)\left(\frac{10.0 \times 10^{-3} \text{ m}}{2}\right)^2 = 15{,}700 \text{ N} \quad (3645 \text{ lb}_\text{f})$$

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8.30 *If a component fabricated from an S-590 alloy (Figure 8.30) is to be exposed to a tensile stress of 300 MPa (43,500 psi) at 650°C (1200°F), estimate its rupture lifetime.*

Solution

This problem asks us to calculate the rupture lifetime of a component fabricated from an S-590 alloy exposed to a tensile stress of 300 MPa at 650°C. All that we need do is read from the 650°C line in Figure 8.30 the rupture lifetime at 300 MPa; this value is about 600 h.

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8.31 *A cylindrical component constructed from an S-590 alloy (Figure 8.30) has a diameter of 12 mm (0.50 in.). Determine the maximum load that may be applied for it to survive 500 h at 925°C (1700°F).*

Solution

We are asked in this problem to determine the maximum load that may be applied to a cylindrical S-590 alloy component that must survive 500 h at 925°C. From Figure 8.30, the stress corresponding to 500 h is about 50 MPa (7,250 psi). Since stress is defined in Equation 6.1 as $\sigma = F/A_0$, and for a cylindrical specimen, $A_0 = \pi\left(\frac{d_0}{2}\right)^2$, then

$$F = \sigma A_0 = \sigma\pi\left(\frac{d_0}{2}\right)^2$$

$$= \left(50 \times 10^6 \text{ N/m}^2\right)(\pi)\left(\frac{12 \times 10^{-3} \text{ m}}{2}\right)^2 = 5655 \text{ N} \quad (1424 \text{ lb}_\text{f})$$

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8.32 *From Equation 8.19, if the logarithm of $\dot{\varepsilon}_s$ is plotted versus the logarithm of σ, then a straight line should result, the slope of which is the stress exponent n. Using Figure 8.31, determine the value of n for the S-590 alloy at 925°C, and for the initial (i.e., lower-temperature) straight line segments at each of 650°C, 730°C, and 815°C.*

Solution

The slope of the line from a log $\dot{\varepsilon}_s$ versus log σ plot yields the value of *n* in Equation 8.19; that is

$$n = \frac{\Delta \log \dot{\varepsilon}_s}{\Delta \log \sigma}$$

We are asked to determine the values of *n* for the creep data at the four temperatures in Figure 8.31 [i.e., at 925°C, and for the initial (i.e., lower-temperature) straight line segments at each of 650°C, 730°C, and 815°C]. This is accomplished by taking ratios of the differences between two log $\dot{\varepsilon}_s$ and log σ values. (Note: Figure 8.31 plots log σ versus log $\dot{\varepsilon}_s$; therefore, values of *n* are equal to the reciprocals of the slopes of the straight-line segments.)

Thus for 650°C

$$n = \frac{\Delta \log \dot{\varepsilon}_s}{\Delta \log \sigma} = \frac{\log\left(10^{-1}\right) - \log\left(10^{-5}\right)}{\log (545\ \text{MPa}) - \log (240\ \text{MPa})} = 11.2$$

While for 730°C

$$n = \frac{\Delta \log \dot{\varepsilon}_s}{\Delta \log \sigma} = \frac{\log (1) - \log\left(10^{-6}\right)}{\log (430\ \text{MPa}) - \log (125\ \text{MPa})} = 11.2$$

And at 815°C

$$n = \frac{\Delta \log \dot{\varepsilon}_s}{\Delta \log \sigma} = \frac{\log (1) - \log\left(10^{-6}\right)}{\log (320\ \text{MPa}) - \log (65\ \text{MPa})} = 8.7$$

And, finally at 925°C

$$n = \frac{\Delta \log \dot{\varepsilon}_s}{\Delta \log \sigma} = \frac{\log\left(10^{2}\right) - \log\left(10^{-5}\right)}{\log (350\ \text{MPa}) - \log (44\ \text{MPa})} = 7.8$$

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8.33 *(a) Estimate the activation energy for creep (i.e., Q_c in Equation 8.20) for the S-590 alloy having the steady-state creep behavior shown in Figure 8.31. Use data taken at a stress level of 300 MPa (43,500 psi) and temperatures of 650°C and 730°C . Assume that the stress exponent n is independent of temperature. (b) Estimate $\dot{\varepsilon}_s$ at 600°C (873 K) and 300 MPa.*

Solution

(a) We are asked to estimate the activation energy for creep for the S-590 alloy having the steady-state creep behavior shown in Figure 8.31, using data taken at σ = 300 MPa and temperatures of 650°C and 730°C. Since σ is a constant, Equation 8.20 takes the form

$$\dot{\varepsilon}_s = K_2 \sigma^n \exp\left(-\frac{Q_c}{RT}\right) = K_2' \exp\left(-\frac{Q_c}{RT}\right)$$

where K_2' is now a constant. (Note: the exponent n has about the same value at these two temperatures per Problem 8.32.) Taking natural logarithms of the above expression

$$\ln \dot{\varepsilon}_s = \ln K_2' - \frac{Q_c}{RT}$$

For the case in which we have creep data at two temperatures (denoted as T_1 and T_2) and their corresponding steady-state creep rates ($\dot{\varepsilon}_{s_1}$ and $\dot{\varepsilon}_{s_2}$), it is possible to set up two simultaneous equations of the form as above, with two unknowns, namely K_2' and Q_c. Solving for Q_c yields

$$Q_c = -\frac{R\left(\ln \dot{\varepsilon}_{s_1} - \ln \dot{\varepsilon}_{s_2}\right)}{\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

Let us choose T_1 as 650°C (923 K) and T_2 as 730°C (1003 K); then from Figure 8.31, at σ = 300 MPa, $\dot{\varepsilon}_{s_1} = 8.9 \times 10^{-5}$ h^{-1} and $\dot{\varepsilon}_{s_2} = 1.3 \times 10^{-2}$ h^{-1}. Substitution of these values into the above equation leads to

$$Q_c = -\frac{(8.31 \text{ J/mol-K})\left[\ln\left(8.9 \times 10^{-5}\right) - \ln\left(1.3 \times 10^{-2}\right)\right]}{\left[\frac{1}{923 \text{ K}} - \frac{1}{1003 \text{ K}}\right]}$$

$$= 480{,}000 \text{ J/mol}$$

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(b) We are now asked to estimate $\dot{\varepsilon}_s$ at 600°C (873 K) and 300 MPa. It is first necessary to determine the value of K_2', which is accomplished using the first expression above, the value of Q_c, and one value each of $\dot{\varepsilon}_s$ and T (say $\dot{\varepsilon}_{s_1}$ and T_1). Thus,

$$K_2' = \dot{\varepsilon}_{s_1} \exp\left(\frac{Q_c}{RT_1}\right)$$

$$= \left(8.9 \times 10^{-5}\ \text{h}^{-1}\right)\exp\left[\frac{480{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(923\ \text{K})}\right] = 1.34 \times 10^{23}\ \text{h}^{-1}$$

Now it is possible to calculate $\dot{\varepsilon}_s$ at 600°C (873 K) and 300 MPa as follows:

$$\dot{\varepsilon}_s = K_2' \exp\left(-\frac{Q_c}{RT}\right)$$

$$= \left(1.34 \times 10^{23}\ \text{h}^{-1}\right)\exp\left[-\frac{480{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(873\ \text{K})}\right]$$

$$= 2.47 \times 10^{-6}\ \text{h}^{-1}$$

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8.34 *Steady-state creep rate data are given below for nickel at 1000°C (1273 K):*

$\dot{\varepsilon}_s$ (s^{-1})	σ [*MPa* (*psi*)]
10^{-4}	15 (2175)
10^{-6}	4.5 (650)

If it is known that the activation energy for creep is 272,000 J/mol, compute the steady-state creep rate at a temperature of 850°C (1123 K) and a stress level of 25 MPa (3625 psi).

Solution

Taking natural logarithms of both sides of Equation 8.20 yields

$$\ln \dot{\varepsilon}_s = \ln K_2 + n \ln \sigma - \frac{Q_c}{RT}$$

With the given data there are two unknowns in this equation--namely K_2 and n. Using the data provided in the problem statement we can set up two independent equations as follows:

$$\ln\left(1 \times 10^{-4}\ \text{s}^{-1}\right) = \ln K_2 + n \ln(15\ \text{MPa}) - \frac{272{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1273\ \text{K})}$$

$$\ln\left(1 \times 10^{-6}\ \text{s}^{-1}\right) = \ln K_2 + n \ln(4.5\ \text{MPa}) - \frac{272{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1273\ \text{K})}$$

Now, solving simultaneously for n and K_2 leads to $n = 3.825$ and $K_2 = 466\ \text{s}^{-1}$. Thus it is now possible to solve for $\dot{\varepsilon}_s$ at 25 MPa and 1123 K using Equation 8.20 as

$$\dot{\varepsilon}_s = K_2 \sigma^n \exp\left(-\frac{Q_c}{RT}\right)$$

$$= \left(466\ \text{s}^{-1}\right)(25\ \text{MPa})^{3.825} \exp\left[-\frac{272{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1123\ \text{K})}\right]$$

$$2.28 \times 10^{-5}\ \text{s}^{-1}$$

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8.35 *Steady-state creep data taken for a stainless steel at a stress level of 70 MPa (10,000 psi) are given as follows:*

$\dot{\varepsilon}_s$ (s^{-1})	T (K)
1.0×10^{-5}	977
2.5×10^{-3}	1089

If it is known that the value of the stress exponent n for this alloy is 7.0, compute the steady-state creep rate at 1250 K and a stress level of 50 MPa (7250 psi).

Solution

Taking natural logarithms of both sides of Equation 8.20 yields

$$\ln \dot{\varepsilon}_s = \ln K_2 + n \ln \sigma - \frac{Q_c}{RT}$$

With the given data there are two unknowns in this equation--namely K_2 and Q_c. Using the data provided in the problem statement we can set up two independent equations as follows:

$$\ln\left(1.0 \times 10^{-5}\ \text{s}^{-1}\right) = \ln K_2 + (7.0)\ln(70\ \text{MPa}) - \frac{Q_c}{(8.31\ \text{J/mol - K})(977\ \text{K})}$$

$$\ln\left(2.5 \times 10^{-3}\ \text{s}^{-1}\right) = \ln K_2 + (7.0)\ln(70\ \text{MPa}) - \frac{Q_c}{(8.31\ \text{J/mol - K})(1089\ \text{K})}$$

Now, solving simultaneously for K_2 and Q_c leads to $K_2 = 2.55 \times 10^5\ \text{s}^{-1}$ and $Q_c = 436{,}000$ J/mol. Thus, it is now possible to solve for $\dot{\varepsilon}_s$ at 50 MPa and 1250 K using Equation 8.20 as

$$\dot{\varepsilon}_s = K_2 \sigma^n \exp\left(-\frac{Q_c}{RT}\right)$$

$$= \left(2.55 \times 10^5\ \text{s}^{-1}\right)(50\ \text{MPa})^{7.0} \exp\left[-\frac{436{,}000\ \text{J/mol}}{(8.31\ \text{J/mol - K})(1250\ \text{K})}\right]$$

$$0.118\ \text{s}^{-1}$$

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Alloys for High-Temperature Use

8.36 *Cite three metallurgical/processing techniques that are employed to enhance the creep resistance of metal alloys.*

Solution

Three metallurgical/processing techniques that are employed to enhance the creep resistance of metal alloys are (1) solid solution alloying, (2) dispersion strengthening by using an insoluble second phase, and (3) increasing the grain size or producing a grain structure with a preferred orientation.

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DESIGN PROBLEMS

8.D1 *Each student (or group of students) is to obtain an object/structure/component that has failed. It may come from your home, an automobile repair shop, a machine shop, etc. Conduct an investigation to determine the cause and type of failure (i.e., simple fracture, fatigue, creep). In addition, propose measures that can be taken to prevent future incidents of this type of failure. Finally, submit a report that addresses the above issues.*

Each student or group of students is to submit their own report on a failure analysis investigation that was conducted.

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Principles of Fracture Mechanics

8.D2 *(a) For the thin-walled spherical tank discussed in Design Example 8.1, on the basis of critical crack size criterion [as addressed in part (a)], rank the following polymers from longest to shortest critical crack length: nylon 6,6 (50% relative humidity), polycarbonate, poly(ethylene terephthalate), and poly(methyl methacrylate). Comment on the magnitude range of the computed values used in the ranking relative to those tabulated for metal alloys as provided in Table 8.3. For these computations, use data contained in Tables B.4 and B.5 in Appendix B.*

(b) Now rank these same four polymers relative to maximum allowable pressure according to the leak-before-break criterion, as described in the (b) portion of Design Example 8.1. As above, comment on these values in relation to those for the metal alloys that are tabulated in Table 8.4.

Solution

(a) This portion of the problem calls for us to rank four polymers relative to critical crack length in the wall of a spherical pressure vessel. In the development of Design Example 8.1, it was noted that critical crack length is proportional to the square of the K_{Ic}–σ_y ratio. Values of K_{Ic} and σ_y as taken from Tables B.4 and B.5 are tabulated below. (Note: when a range of σ_y or K_{Ic} values is given, the average value is used.)

Material	K_{Ic} $\left(\text{MPa}\sqrt{\text{m}}\right)$	σ_y (MPa)
Nylon 6,6	2.75	51.7
Polycarbonate	2.2	62.1
Poly(ethylene terephthlate)	5.0	59.3
Poly(methyl methacrylate)	1.2	63.5

On the basis of these values, the four polymers are ranked per the squares of the K_{Ic}–σ_y ratios as follows:

Material	$\left(\frac{K_{Ic}}{\sigma_y}\right)^2$ (mm)
PET	7.11
Nylon 6,6	2.83
PC	1.26
PMMA	0.36

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These values are smaller than those for the metal alloys given in Table 8.3, which range from 0.93 to 43.1 mm.

(b) Relative to the leak-before-break criterion, the $K_{Ic}^2 - \sigma_y$ ratio is used. The four polymers are ranked according to values of this ratio as follows:

Material	$\frac{K_{Ic}^2}{\sigma_y}$ (MPa - m)
PET	0.422
Nylon 6,6	0.146
PC	0.078
PMMA	0.023

These values are all smaller than those for the metal alloys given in Table 8.4, which values range from 1.2 to 11.2 MPa-m.

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Data Extrapolation Methods

8.D3 *An S-590 alloy component (Figure 8.32) must have a creep rupture lifetime of at least 100 days at 500°C (773 K). Compute the maximum allowable stress level.*

Solution

This problem asks that we compute the maximum allowable stress level to give a rupture lifetime of 100 days for an S-590 iron component at 773 K. It is first necessary to compute the value of the Larson-Miller parameter as follows:

$$T\left(20 + \log t_r\right) = (773\ \text{K})\left\{20 + \log\left[(100\ \text{days})(24\ \text{h/day})\right]\right\}$$

$$= 18.1 \times 10^3$$

From the curve in Figure 8.32, this value of the Larson-Miller parameter corresponds to a stress level of about 530 MPa (77,000 psi).

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8.D4 *Consider an S-590 alloy component (Figure 8.32) that is subjected to a stress of 200 MPa (29,000 psi). At what temperature will the rupture lifetime be 500 h?*

Solution

We are asked in this problem to calculate the temperature at which the rupture lifetime is 500 h when an S-590 iron component is subjected to a stress of 200 MPa (29,000 psi). From the curve shown in Figure 8.32, at 200 MPa, the value of the Larson-Miller parameter is 22.5×10^3 (K-h). Thus,

$$22.5 \times 10^3 \text{ (K - h)} = T\left(20 + \log t_r\right)$$

$$= T\left[20 + \log (500 \text{ h})\right]$$

Or, solving for T yields $T = 991$ K (718°C).

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8.D5 *For an 18-8 Mo stainless steel (Figure 8.35), predict the time to rupture for a component that is subjected to a stress of 80 MPa (11,600 psi) at 700°C (973 K).*

Solution

This problem asks that we determine, for an 18-8 Mo stainless steel, the time to rupture for a component that is subjected to a stress of 80 MPa (11,600 psi) at 700°C (973 K). From Figure 8.35, the value of the Larson-Miller parameter at 80 MPa is about 23.5×10^3, for T in K and t_r in h. Therefore,

$$23.5 \times 10^3 = T(20 + \log t_r)$$

$$= 973(20 + \log t_r)$$

And, solving for t_r

$$24.15 = 20 + \log t_r$$

which leads to $t_r = 1.42 \times 10^4$ h = 1.6 yr.

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8.D6 *Consider an 18-8 Mo stainless steel component (Figure 8.35) that is exposed to a temperature of 500°C (773 K). What is the maximum allowable stress level for a rupture lifetime of 5 years? 20 years?*

Solution

We are asked in this problem to calculate the stress levels at which the rupture lifetime will be 5 years and 20 years when an 18-8 Mo stainless steel component is subjected to a temperature of 500°C (773 K). It first becomes necessary to calculate the value of the Larson-Miller parameter for each time. The values of t_r corresponding to 5 and 20 years are 4.38×10^4 h and 1.75×10^5 h, respectively. Hence, for a lifetime of 5 years

$$T\left(20 + \log t_r\right) = 773\left[20 + \log\left(4.38 \times 10^4\right)\right] = 19.05 \times 10^3$$

And for $t_r = 20$ years

$$T\left(20 + \log t_r\right) = 773\left[20 + \log\left(1.75 \times 10^5\right)\right] = 19.51 \times 10^3$$

Using the curve shown in Figure 8.35, the stress values corresponding to the five- and twenty-year lifetimes are approximately 260 MPa (37,500 psi) and 225 MPa (32,600 psi), respectively.

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CHAPTER 9

PHASE DIAGRAMS

PROBLEM SOLUTIONS

Solubility Limit

9.1 *Consider the sugar–water phase diagram of Figure 9.1.*

(a) How much sugar will dissolve in 1500 g water at 90°C (194°F)?

(b) If the saturated liquid solution in part (a) is cooled to 20°C (68°F), some of the sugar will precipitate out as a solid. What will be the composition of the saturated liquid solution (in wt% sugar) at 20°C?

(c) How much of the solid sugar will come out of solution upon cooling to 20°C?

Solution

(a) We are asked to determine how much sugar will dissolve in 1000 g of water at 90°C. From the solubility limit curve in Figure 9.1, at 90°C the maximum concentration of sugar in the syrup is about 77 wt%. It is now possible to calculate the mass of sugar using Equation 4.3 as

$$C_{\text{sugar}}(\text{wt\%}) = \frac{m_{\text{sugar}}}{m_{\text{sugar}} + m_{\text{water}}} \times 100$$

$$77\ \text{wt\%} = \frac{m_{\text{sugar}}}{m_{\text{sugar}} + 1500\ \text{g}} \times 100$$

Solving for m_{sugar} yields $m_{\text{sugar}} = 5022$ g

(b) Again using this same plot, at 20°C the solubility limit (or the concentration of the saturated solution) is about 64 wt% sugar.

(c) The mass of sugar in this saturated solution at 20°C (m'_{sugar}) may also be calculated using Equation 4.3 as follows:

$$64\ \text{wt\%} = \frac{m'_{\text{sugar}}}{m'_{\text{sugar}} + 1500\ \text{g}} \times 100$$

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which yields a value for m'_{sugar} of 2667 g. Subtracting the latter from the former of these sugar concentrations yields the amount of sugar that precipitated out of the solution upon cooling m''_{sugar}; that is

$$m''_{\text{sugar}} = m_{\text{sugar}} - m\tilde{Q}_{\text{sugar}} = 5022\text{ g} - 2667\text{ g} = 2355\text{ g}$$

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9.2 *At 500°C (930°F), what is the maximum solubility (a) of Cu in Ag? (b) Of Ag in Cu?*

Solution

(a) From Figure 9.7, the maximum solubility of Cu in Ag at 500°C corresponds to the position of the β–(α + β) phase boundary at this temperature, or to about 2 wt% Cu.

(b) From this same figure, the maximum solubility of Ag in Cu corresponds to the position of the α–(α + β) phase boundary at this temperature, or about 1.5 wt% Ag.

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Microstructure

9.3 *Cite three variables that determine the microstructure of an alloy.*

Solution

Three variables that determine the microstructure of an alloy are (1) the alloying elements present, (2) the concentrations of these alloying elements, and (3) the heat treatment of the alloy.

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Phase Equilibria

9.4 *What thermodynamic condition must be met for a state of equilibrium to exist?*

Solution

In order for a system to exist in a state of equilibrium the free energy must be a minimum for some specified combination of temperature, pressure, and composition.

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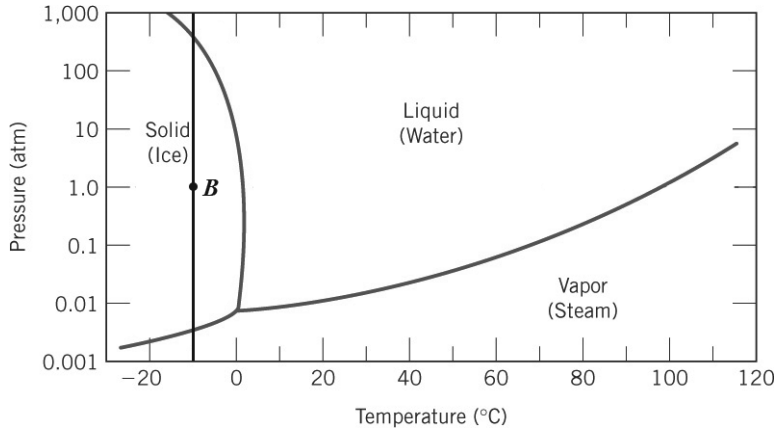
One-Component (or Unary) Phase Diagrams

9.5 *Consider a specimen of ice that is at 210°C and 1 atm pressure. Using Figure 9.2, the pressure–temperature phase diagram for H_2O, determine the pressure to which the specimen must be raised or lowered to cause it (a) to melt, and (b) to sublime.*

Solution

The figure below shows the pressure-temperature phase diagram for H_2O, Figure 10.2; a vertical line has been constructed at -10°C, and the location on this line at 1 atm pressure (point *B*) is also noted.



(a) Melting occurs, (by changing pressure) as, moving vertically (upward) at this temperature, we cross the Ice-Liquid phase boundary. This occurs at approximately 570 atm; thus, the pressure of the specimen must be raised from 1 to 570 atm.

(b) In order to determine the pressure at which sublimation occurs at this temperature, we move vertically downward from 1 atm until we cross the Ice-Vapor phase boundary. This intersection occurs at approximately 0.0023 atm.

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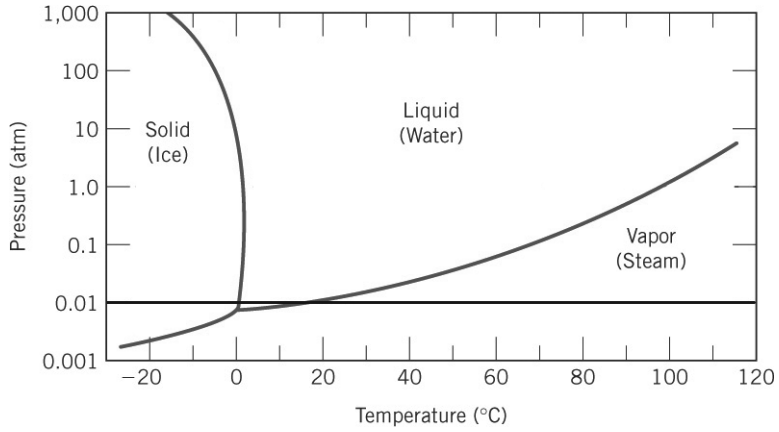
9.6 *At a pressure of 0.01 atm, determine (a) the melting temperature for ice, and (b) the boiling temperature for water.*

Solution

The melting temperature for ice and the boiling temperature for water at a pressure of 0.01 atm may be determined from the pressure-temperature diagram for this system, Figure 10.2, which is shown below; a horizontal line has been constructed across this diagram at a pressure of 0.01 atm.



The melting and boiling temperatures for ice at a pressure of 0.01 atm may be determined by moving horizontally across the pressure-temperature diagram at this pressure. The temperature corresponding to the intersection of the Ice-Liquid phase boundary is the melting temperature, which is approximately 1°C. On the other hand, the boiling temperature is at the intersection of the horizontal line with the Liquid-Vapor phase boundary--approximately 16°C.

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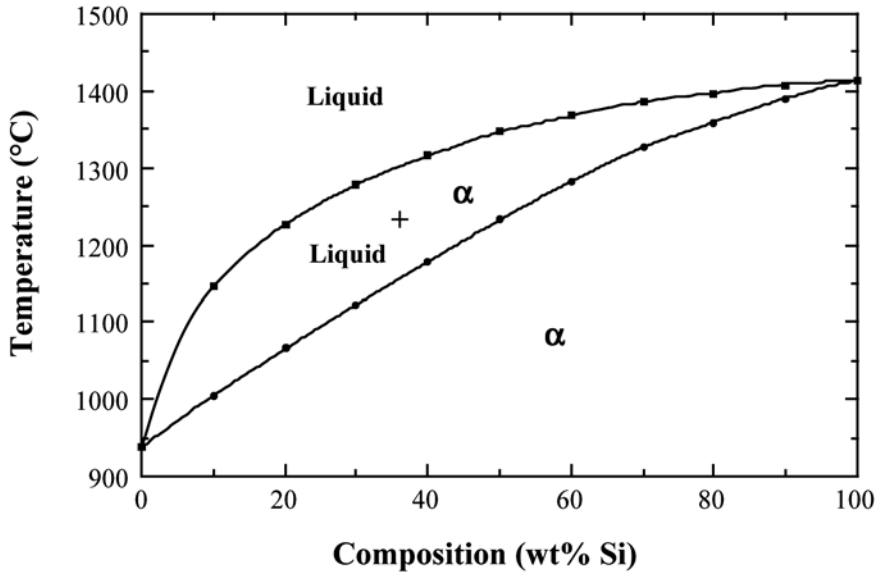
Binary Isomorphous Systems

9.7 *Given here are the solidus and liquidus temperatures for the germanium-silicon system. Construct the phase diagram for this system and label each region.*

***Composition* (*wt% Si*)**	***Solidus Temperature* (°*C*)**	***Liquidus Temperature* (°*C*)**
0	*938*	*938*
10	*1005*	*1147*
20	*1065*	*1226*
30	*1123*	*1278*
40	*1178*	*1315*
50	*1232*	*1346*
60	*1282*	*1367*
70	*1326*	*1385*
80	*1359*	*1397*
90	*1390*	*1408*
100	*1414*	*1414*

Solution

The germanium-silicon phase diagram is constructed below.



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Interpretation of Phase Diagrams

9.8 *Cite the phases that are present and the phase compositions for the following alloys:*

(a) 90 wt% Zn-10 wt% Cu at 400°C (750°F)

(b) 75 wt% Sn-25 wt% Pb at 175°C (345°F)

(c) 55 wt% Ag-45 wt% Cu at 900°C (1650°F)

(d) 30 wt% Pb-70 wt% Mg at 425°C (795°F)

(e) 2.12 kg Zn and 1.88 kg Cu at 500°C (930°F)

(f) 37 lb_m Pb and 6.5 lb_m Mg at 400°C (750°F)

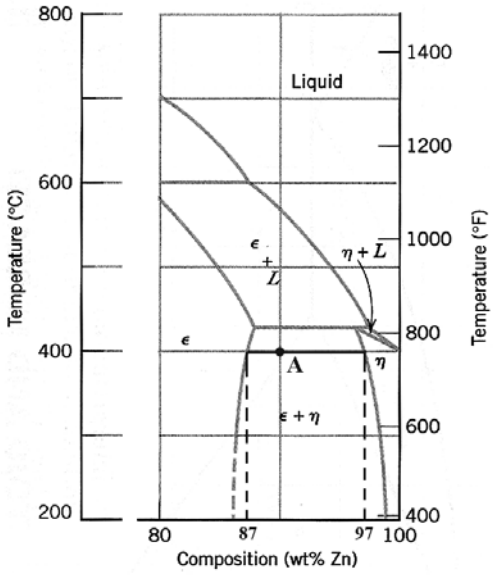
(g) 8.2 mol Ni and 4.3 mol Cu at 1250°C (2280°F)

(h) 4.5 mol Sn and 0.45 mol Pb at 200°C (390°F)

Solution

This problem asks that we cite the phase or phases present for several alloys at specified temperatures.

(a) That portion of the Cu-Zn phase diagram (Figure 9.19) that pertains to this problem is shown below; the point labeled "A" represents the 90 wt% Zn-10 wt% Cu composition at 400°C.



As may be noted, point A lies within the ε and η phase field. A tie line has been constructed at 400°C; its intersection with the ε–ε + η phase boundary is at 87 wt% Zn, which corresponds to the composition of the ε phase. Similarly, the tie-line intersection with the ε + η–η phase boundary occurs at 97 wt% Zn, which is the composition of the η phase. Thus, the phase compositions are as follows:

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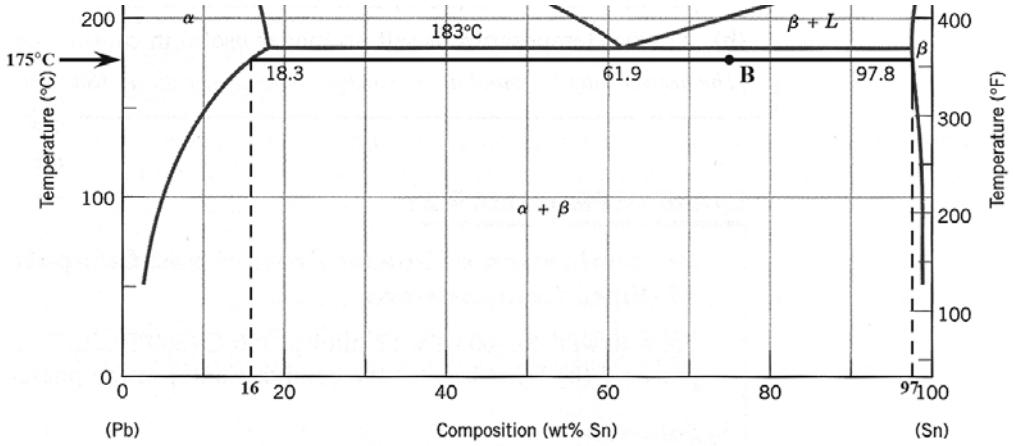
$$C_\varepsilon = 87 \text{ wt\% Zn-13 wt\% Cu}$$

$$C_\eta = 97 \text{ wt\% Zn-3 wt\% Cu}$$

(b) That portion of the Pb-Sn phase diagram (Figure 9.8) that pertains to this problem is shown below; the point labeled "B" represents the 75 wt% Sn-25 wt% Pb composition at 175°C.



As may be noted, point B lies within the α + β phase field. A tie line has been constructed at 175°C; its intersection with the α–α + β phase boundary is at 16 wt% Sn, which corresponds to the composition of the α phase. Similarly, the tie-line intersection with the α + β–β phase boundary occurs at 97 wt% Sn, which is the composition of the β phase. Thus, the phase compositions are as follows:

$$C_\alpha = 16 \text{ wt\% Sn-84 wt\% Pb}$$

$$C_\beta = 97 \text{ wt\% Sn-3 wt\% Pb}$$

(c) The Ag-Cu phase diagram (Figure 9.7) is shown below; the point labeled "C" represents the 55 wt% Ag-45 wt% Cu composition at 900°C.

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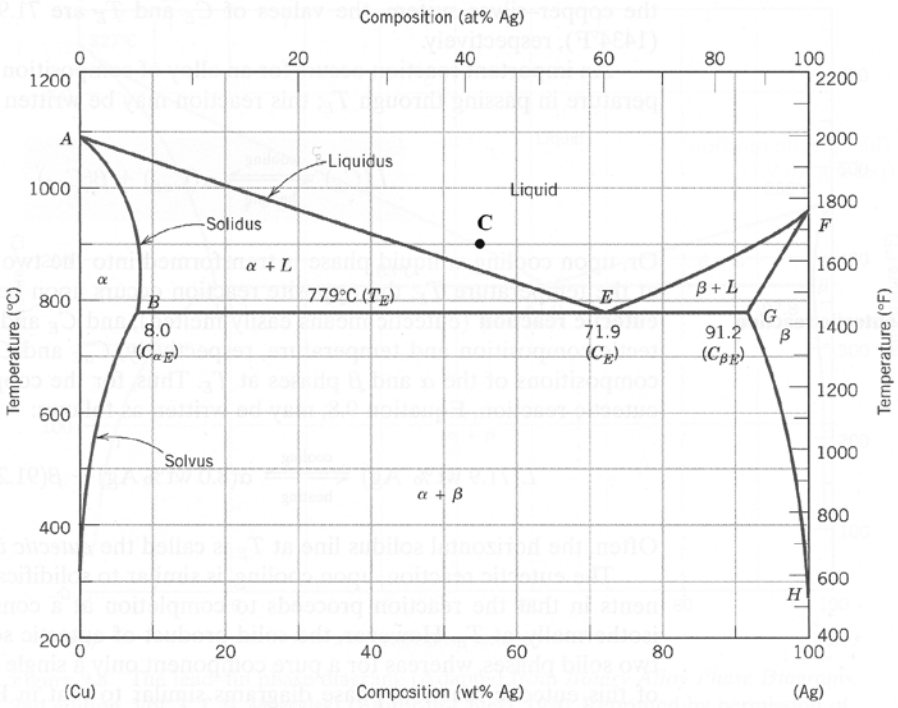

As may be noted, point C lies within the Liquid phase field. Therefore, only the liquid phase is present; its composition is 55 wt% Ag-45 wt% Cu.

(d) The Mg-Pb phase diagram (Figure 9.20) is shown below; the point labeled "D" represents the 30 wt% Pb-70 wt% Mg composition at 425°C.

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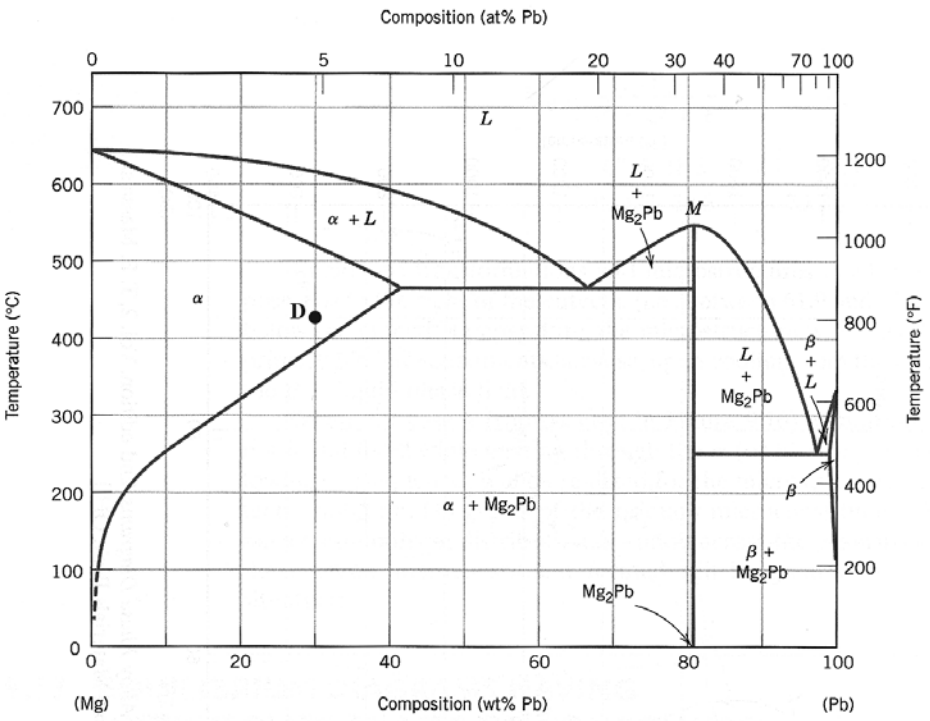

As may be noted, point D lies within the α phase field. Therefore, only the α phase is present; its composition is 30 wt% Pb-70 wt% Mg.

(e) For an alloy composed of 2.12 kg Zn and 1.88 kg Cu and at 500°C, we must first determine the Zn and Cu concentrations, as

$$C_{Zn} = \frac{2.12\ \text{kg}}{2.12\ \text{kg} + 1.88\ \text{kg}} \times 100 = 53\ \text{wt\%}$$

$$C_{Cu} = \frac{1.88\ \text{kg}}{2.12\ \text{kg} + 1.88\ \text{kg}} \times 100 = 47\ \text{wt\%}$$

That portion of the Cu-Zn phase diagram (Figure 9.19) that pertains to this problem is shown below; the point labeled "E" represents the 53 wt% Zn-47 wt% Cu composition at 500°C.

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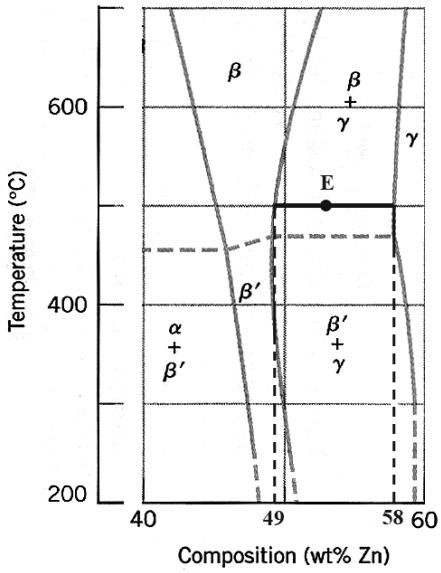

As may be noted, point E lies within the β + γ phase field. A tie line has been constructed at 500°C; its intersection with the β–β + γ phase boundary is at 49 wt% Zn, which corresponds to the composition of the β phase. Similarly, the tie-line intersection with the β + γ–γ phase boundary occurs at 58 wt% Zn, which is the composition of the γ phase. Thus, the phase compositions are as follows:

$$C_\beta = 49 \text{ wt\% Zn-51 wt\% Cu}$$

$$C_\gamma = 58 \text{ wt\% Zn-42 wt\% Cu}$$

(f) For an alloy composed of 37 lb_m Pb and 6.5 lb_m Mg and at 400°C, we must first determine the Pb and Mg concentrations, as

$$C_{Pb} = \frac{37 \text{ lb}_m}{37 \text{ lb}_m + 6.5 \text{ lb}_m} \times 100 = 85 \text{ wt\%}$$

$$C_{Mg} = \frac{6.5 \text{ lb}_m}{37 \text{ lb}_m + 6.5 \text{ lb}_m} \times 100 = 15 \text{ wt\%}$$

That portion of the Mg-Pb phase diagram (Figure 9.20) that pertains to this problem is shown below; the point labeled "F" represents the 85 wt% Pb-15 wt% Mg composition at 400°C.

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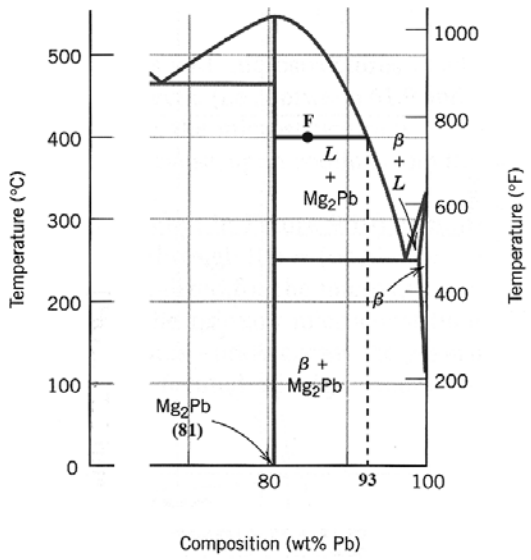

As may be noted, point F lies within the L + Mg_2Pb phase field. A tie line has been constructed at 400°C; it intersects the vertical line at 81 wt% Pb, which corresponds to the composition of Mg_2Pb. Furthermore, the tie line intersection with the L + Mg_2Pb-L phase boundary is at 93 wt% Pb, which is the composition of the liquid phase. Thus, the phase compositions are as follows:

$$C_{Mg_2Pb} = 81 \text{ wt\% Pb-19 wt\% Mg}$$

$$C_L = 93 \text{ wt\% Pb-7 wt\% Mg}$$

(g) For an alloy composed of 8.2 mol Ni and 4.3 mol Cu and at 1250°C, it is first necessary to determine the Ni and Cu concentrations, which we will do in wt% as follows:

$$n'_{Ni} = n_{m_{Ni}} A_{Ni} = (8.2 \text{ mol})(58.69 \text{ g/mol}) = 481.3 \text{ g}$$

$$n'_{Cu} = n_{m_{Cu}} A_{Cu} = (4.3 \text{ mol})(63.55 \text{ g/mol}) = 273.3 \text{ g}$$

$$C_{Ni} = \frac{481.3 \text{ g}}{481.3 \text{ g} + 273.3 \text{ g}} \times 100 = 63.8 \text{ wt\%}$$

$$C_{Cu} = \frac{273.3 \text{ g}}{481.3 \text{ g} + 273.3 \text{ g}} \times 100 = 36.2 \text{ wt\%}$$

The Cu-Ni phase diagram (Figure 9.3*a*) is shown below; the point labeled "G" represents the 63.8 wt% Ni-36.2 wt% Cu composition at 1250°C.

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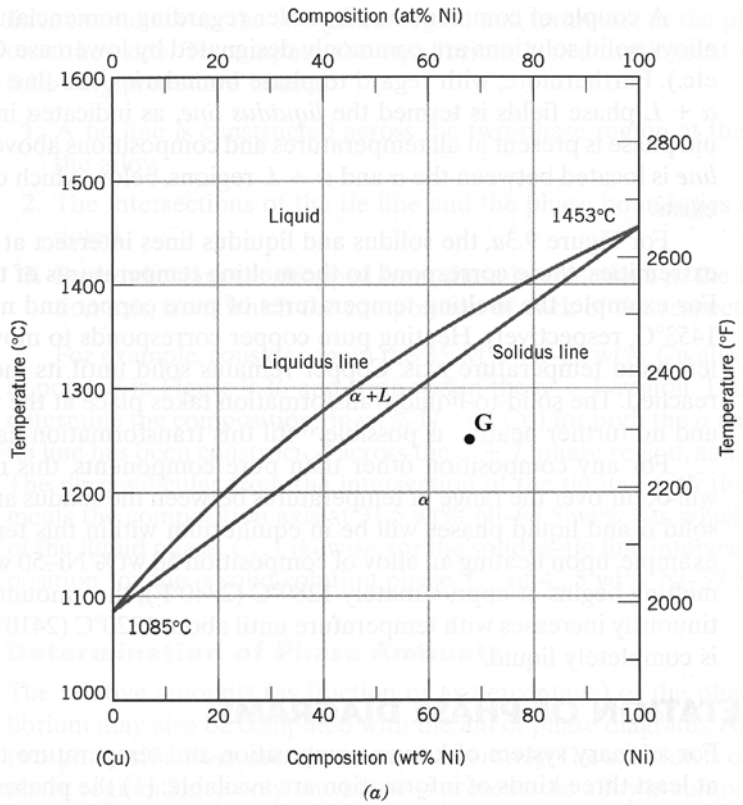

(a)

As may be noted, point G lies within the α phase field. Therefore, only the α phase is present; its composition is 63.8 wt% Ni-36.2 wt% Cu.

(h) For an alloy composed of 4.5 mol Sn and 0.45 mol Pb and at 200°C, it is first necessary to determine the Sn and Pb concentrations, which we will do in weight percent as follows:

$$n'_{\text{Sn}} = n_{m_{\text{Sn}}} A_{\text{Sn}} = (4.5 \text{ mol})(118.71 \text{ g/mol}) = 534.2 \text{ g}$$

$$n'_{\text{Pb}} = n_{m_{\text{Pb}}} A_{\text{Pb}} = (0.45 \text{ mol})(207.2 \text{ g/mol}) = 93.2 \text{ g}$$

$$C_{\text{Sn}} = \frac{534.2 \text{ g}}{534.2 \text{ g} + 93.2 \text{ g}} \times 100 = 85.1 \text{ wt\%}$$

$$C_{\text{Pb}} = \frac{93.2 \text{ g}}{534.2 \text{ g} + 93.2 \text{ g}} \times 100 = 14.9 \text{ wt\%}$$

That portion of the Pb-Sn phase diagram (Figure 9.8) that pertains to this problem is shown below; the point labeled "H" represents the 85.1 wt% Sn-14.9 wt% Pb composition at 200°C.

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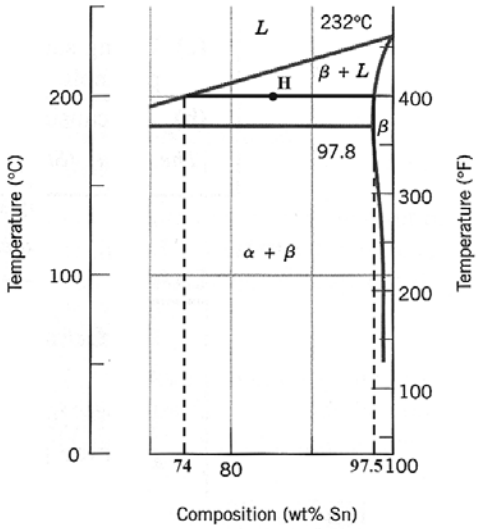

As may be noted, point H lies within the β + *L* phase field. A tie line has been constructed at 200°C; its intersection with the *L*–β + *L* phase boundary is at 74 wt% Sn, which corresponds to the composition of the *L* phase. Similarly, the tie-line intersection with the β + *L*–β phase boundary occurs at 97.5 wt% Sn, which is the composition of the β phase. Thus, the phase compositions are as follows:

$$C_{\beta} = 97.5 \text{ wt\% Sn-2.5 wt\% Pb}$$

$$C_{L} = 74 \text{ wt\% Sn-26 wt\% Pb}$$

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9.9 *Is it possible to have a copper–nickel alloy that, at equilibrium, consists of a liquid phase of composition 20 wt% Ni–80 wt% Cu and also an α phase of composition 37 wt% Ni–63 wt% Cu? If so, what will be the approximate temperature of the alloy? If this is not possible, explain why.*

Solution

It is *not possible* to have a Cu-Ni alloy, which at equilibrium, consists of a liquid phase of composition 20 wt% Ni-80 wt% Cu and an α phase of composition 37 wt% Ni-63 wt% Cu. From Figure 9.3*a*, a single tie line does not exist within the $\alpha + L$ region that intersects the phase boundaries at the given compositions. At 20 wt% Ni, the L-($\alpha + L$) phase boundary is at about 1200°C, whereas at 37 wt% Ni the ($L + \alpha$)-α phase boundary is at about 1230°C.

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9.10 *Is it possible to have a copper-zinc alloy that, at equilibrium, consists of an ε phase of composition 80 wt% Zn-20 wt% Cu, and also a liquid phase of composition 95 wt% Zn-5 wt% Cu? If so, what will be the approximate temperature of the alloy? If this is not possible, explain why.*

Solution

It *is not* possible to have a Cu-Zn alloy, which at equilibrium consists of an ε phase of composition 80 wt% Zn-20 wt% Cu and also a liquid phase of composition 95 wt% Zn-5 wt% Cu. From Figure 9.19 a single tie line does not exist within the ε + *L* region which intersects the phase boundaries at the given compositions. At 80 wt% Zn, the ε-(ε + *L*) phase boundary is at about 575°C, whereas at 95 wt% Zn the (ε + *L*)-*L* phase boundary is at about 490°C.

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9.11 *A copper-nickel alloy of composition 70 wt% Ni-30 wt% Cu is slowly heated from a temperature of 1300°C (2370°F).*

(a) At what temperature does the first liquid phase form?

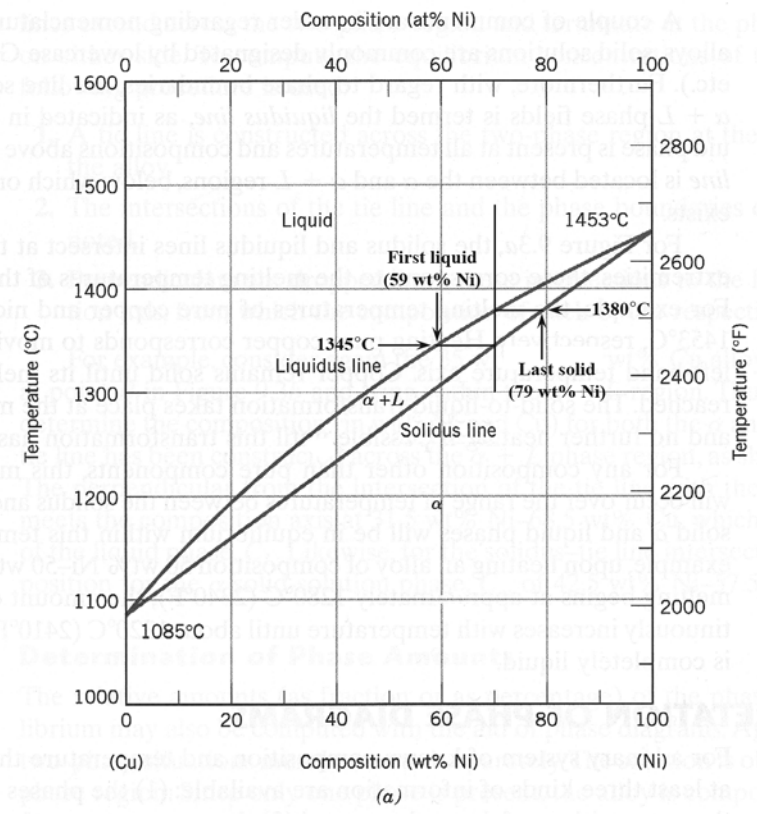
(b) What is the composition of this liquid phase?

(c) At what temperature does complete melting of the alloy occur?

(d) What is the composition of the last solid remaining prior to complete melting?

Solution

Shown below is the Cu-Ni phase diagram (Figure 9.3*a*) and a vertical line constructed at a composition of 70 wt% Ni-30 wt% Cu.



(a) Upon heating from 1300°C, the first liquid phase forms at the temperature at which this vertical line intersects the α-($\alpha + L$) phase boundary--i.e., about 1345°C.

(b) The composition of this liquid phase corresponds to the intersection with the ($\alpha + L$)-L phase boundary, of a tie line constructed across the $\alpha + L$ phase region at 1345°C--i.e., 59 wt% Ni;

(c) Complete melting of the alloy occurs at the intersection of this same vertical line at 70 wt% Ni with the ($\alpha + L$)-L phase boundary--i.e., about 1380°C;

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(d) The composition of the last solid remaining prior to complete melting corresponds to the intersection with α-(α + L) phase boundary, of the tie line constructed across the α + L phase region at 1380°C--i.e., about 79 wt% Ni.

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9.12 *A 50 wt% Pb-50 wt% Mg alloy is slowly cooled from 700°C (1290°F) to 400°C (750°F).*

(a) At what temperature does the first solid phase form?

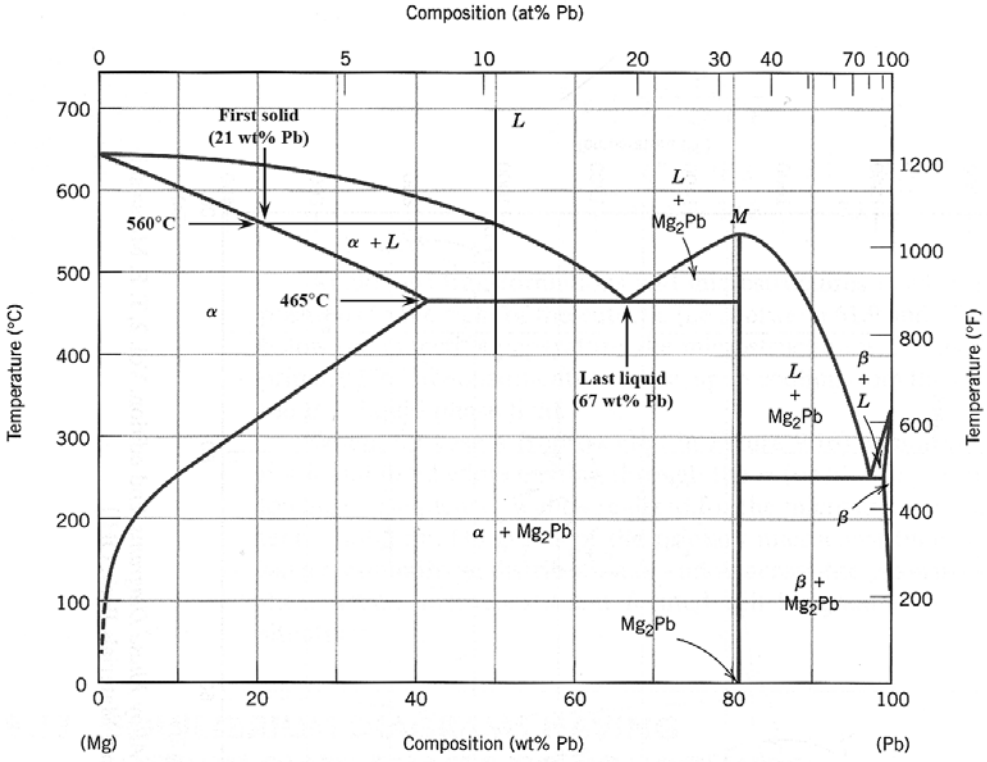
(b) What is the composition of this solid phase?

(c) At what temperature does the liquid solidify?

(d) What is the composition of this last remaining liquid phase?

Solution

Shown below is the Mg-Pb phase diagram (Figure 9.20) and a vertical line constructed at a composition of 50 wt% Pb-50 wt% Mg.



(a) Upon cooling from 700°C, the first solid phase forms at the temperature at which a vertical line at this composition intersects the L-($\alpha + L$) phase boundary--i.e., about 560°C;

(b) The composition of this solid phase corresponds to the intersection with the α-($\alpha + L$) phase boundary, of a tie line constructed across the $\alpha + L$ phase region at 560°C--i.e., 21 wt% Pb-79 wt% Mg;

(c) Complete solidification of the alloy occurs at the intersection of this same vertical line at 50 wt% Pb with the eutectic isotherm--i.e., about 465°C;

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(d) The composition of the last liquid phase remaining prior to complete solidification corresponds to the eutectic composition--i.e., about 67 wt% Pb-33 wt% Mg.

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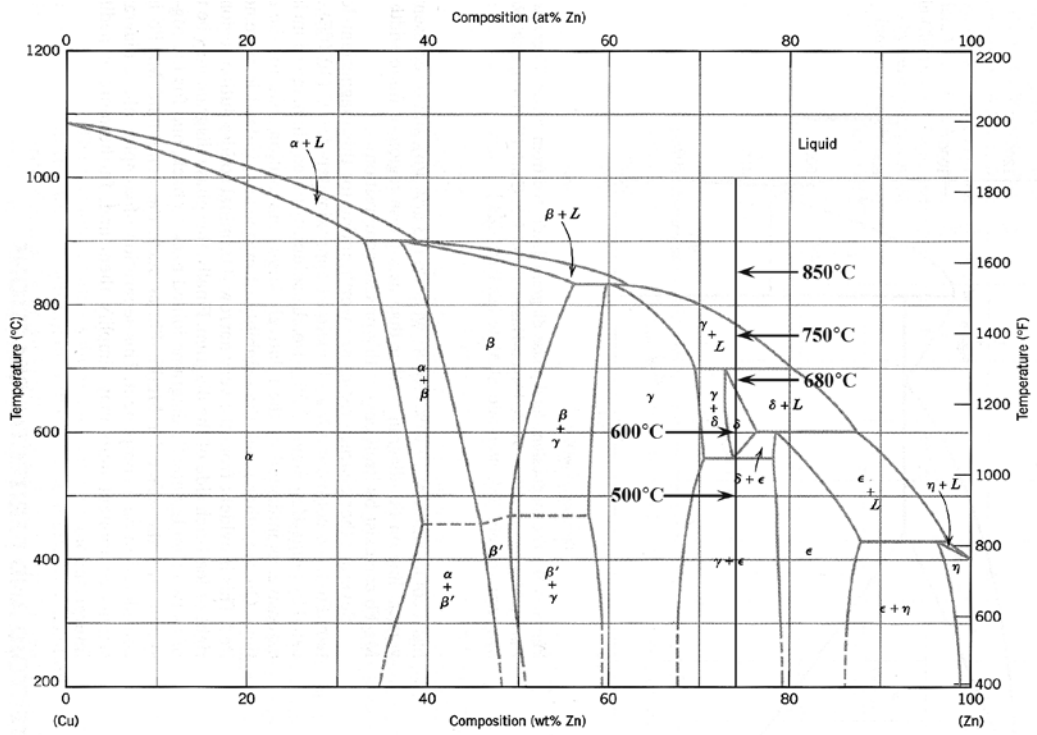
9.13 *For an alloy of composition 74 wt% Zn-26 wt% Cu, cite the phases present and their compositions at the following temperatures: 850°C, 750°C, 680°C, 600°C, and 500°C.*

Solution

This problem asks us to determine the phases present and their concentrations at several temperatures, for an alloy of composition 74 wt% Zn-26 wt% Cu. From Figure 9.19 (the Cu-Zn phase diagram), which is shown below with a vertical line constructed at the specified composition:



At 850°C, a liquid phase is present; C_L = 74 wt% Zn-26 wt% Cu

At 750°C, γ and liquid phases are present; C_γ = 67 wt% Zn-33 wt% Cu; C_L = 77 wt% Zn-23 wt% Cu

At 680°C, δ and liquid phases are present; C_δ = 73 wt% Zn-27 wt% Cu; C_L = 82 wt% Zn-18 wt% Cu

At 600°C, the δ phase is present; C_δ = 74 wt% Zn-26 wt% Cu

At 500°C, γ and ε phases are present; C_γ = 69 wt% Zn-31 wt% Cu; C_ε = 78 wt% Zn-22 wt% Cu

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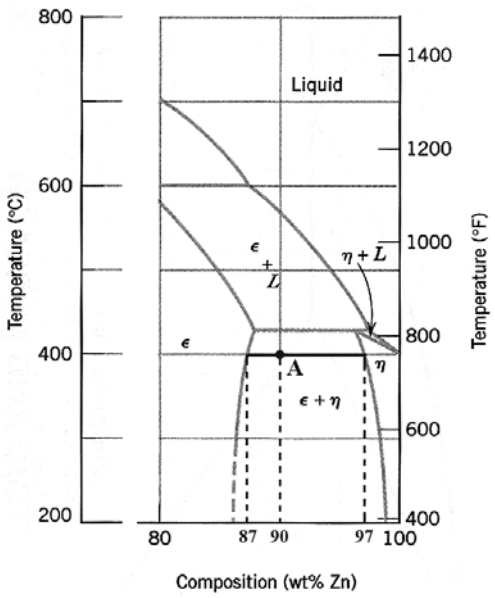
9.14 *Determine the relative amounts (in terms of mass fractions) of the phases for the alloys and temperatures given in Problem 9.8.*

Solution

This problem asks that we determine the phase mass fractions for the alloys and temperatures in Problem 9.8.

(a) From Problem 9.8a, ε and η phases are present for a 90 wt% Zn-10 wt% Cu alloy at 400°C, as represented in the portion of the Cu-Zn phase diagram shown below (at point A).



Furthermore, the compositions of the phases, as determined from the tie line are

C_ε = 87 wt% Zn-13 wt% Cu

C_η = 97 wt% Zn-3 wt% Cu

Inasmuch as the composition of the alloy C_0 = 90 wt% Zn, application of the appropriate lever rule expressions (for compositions in weight percent zinc) leads to

$$W_\varepsilon = \frac{C_\eta - C_0}{C_\eta - C_\varepsilon} = \frac{97 - 90}{97 - 87} = 0.70$$

$$W_\eta = \frac{C_0 - C_\varepsilon}{C_\eta - C_\varepsilon} = \frac{90 - 87}{97 - 87} = 0.30$$

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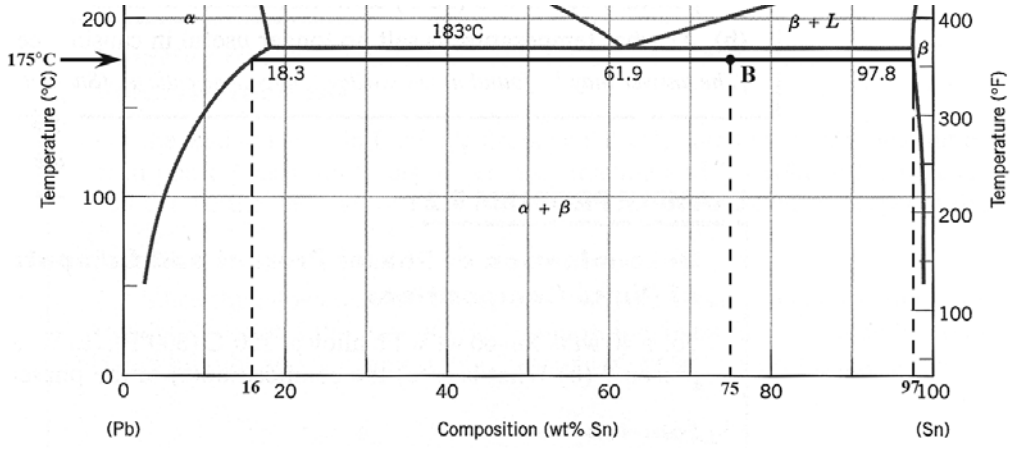
(b) From Problem 9.8b, α and β phases are present for a 75 wt% Sn-25 wt% Pb alloy at 175°C, as represented in the portion of the Pb-Sn phase diagram shown below (at point B).



Furthermore, the compositions of the phases, as determined from the tie line are

C_α = 16 wt% Sn-84 wt% Pb

C_β = 97 wt% Sn-3 wt% Pb

Inasmuch as the composition of the alloy C_0 = 75 wt% Sn, application of the appropriate lever rule expressions (for compositions in weight percent tin) leads to

$$W_\alpha = \frac{C_\beta - C_0}{C_\beta - C_\alpha} = \frac{97 - 75}{97 - 16} = 0.27$$

$$W_\beta = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha} = \frac{75 - 16}{97 - 16} = 0.73$$

(c) From Problem 9.8c, just the liquid phase is present for a 55 wt% Ag-45 wt% Cu alloy at 900°C, as may be noted in the Ag-Cu phase diagram shown below (at point C)—i.e., W_L = 1.0

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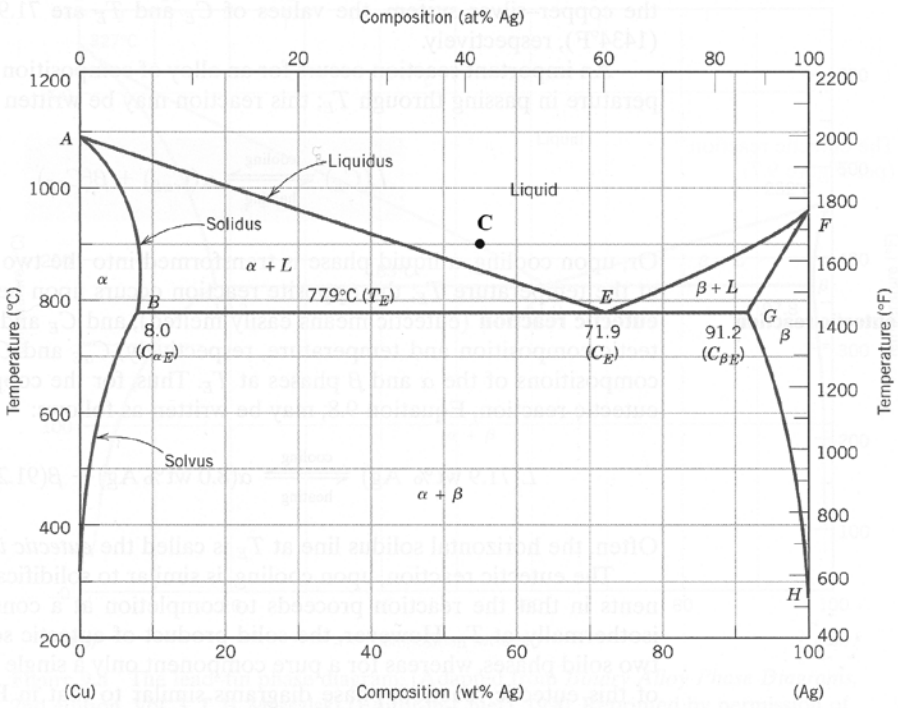
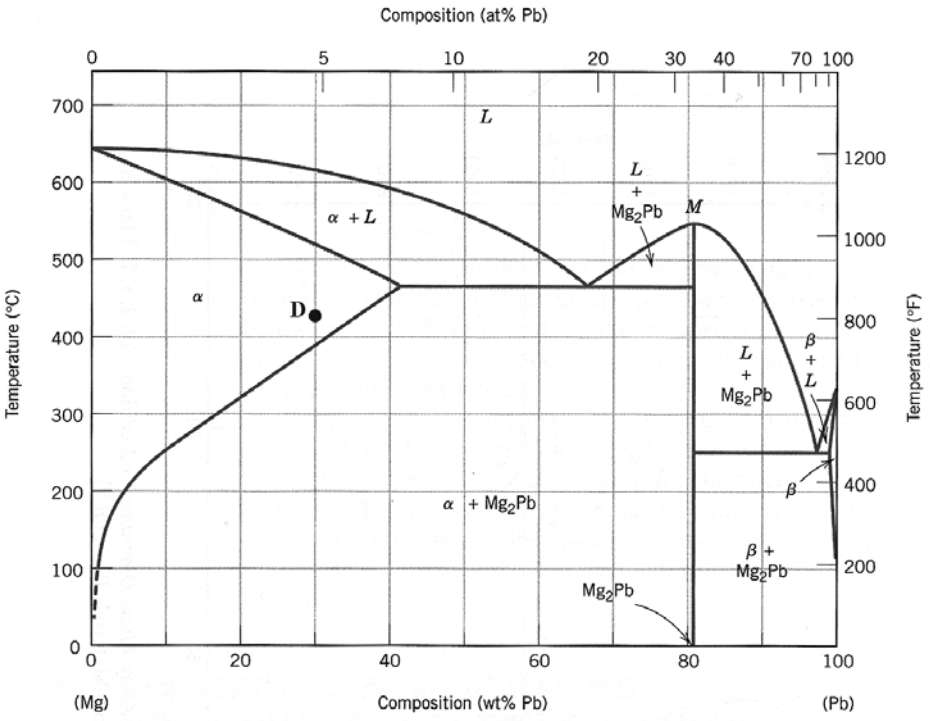


(d) From Problem 9.8d, just the α phase is present for a 30 wt% Pb-70 wt% Mg alloy at 425°C, as may be noted in the Mg-Pb phase diagram shown below (at point D)—i.e., $W_\alpha = 1.0$



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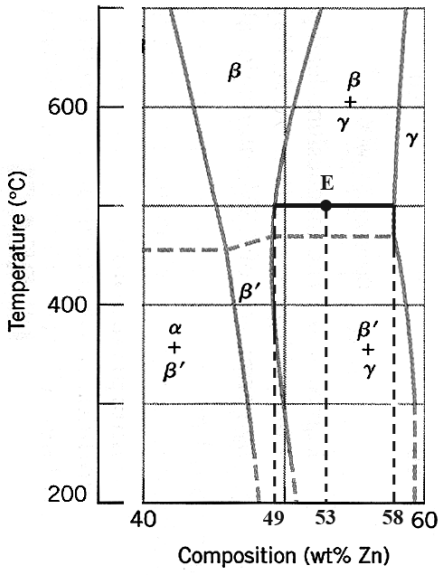
(e) From Problem 9.8e, β and γ phases are present for an alloy composed of 2.12 kg Zn and 1.88 kg Cu (i.e., of composition 53 wt% Zn-47 wt% Cu) at 500°C. This is represented in the portion of the Cu-Zn phase diagram shown below (at point E).



Furthermore, the compositions of the phases, as determined from the tie line are

C_β = 49 wt% Zn-51 wt% Cu

C_γ = 58 wt% Zn-42 wt% Cu

Inasmuch as the composition of the alloy C_0 = 53 wt% Zn and application of the appropriate lever rule expressions (for compositions in weight percent zinc) leads to

$$W_\beta = \frac{C_\gamma - C_0}{C_\gamma - C_\beta} = \frac{58 - 53}{58 - 49} = 0.56$$

$$W_\gamma = \frac{C_0 - C_\beta}{C_\gamma - C_\beta} = \frac{53 - 49}{58 - 49} = 0.44$$

(f) From Problem 9.8f, *L* and Mg_2Pb phases are present for an alloy composed of 37 lb_m Pb and 6.5 lb_m Mg (85 wt% Pb-15 wt% Mg) at 400°C. This is represented in the portion of the Pb-Mg phase diagram shown below (at point F).

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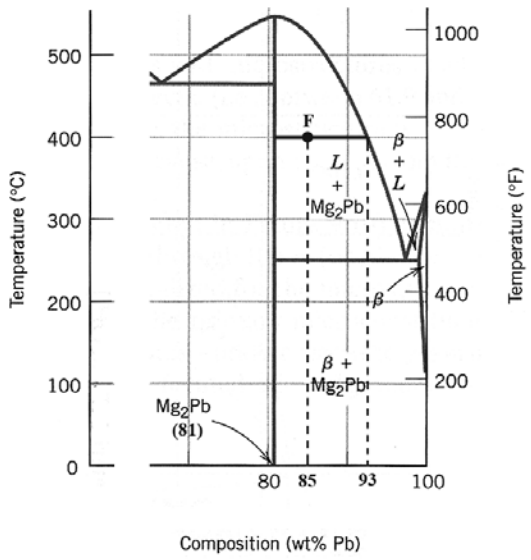

Furthermore, the compositions of the phases, as determined from the tie line are

C_{Mg_2Pb} = 81 wt% Pb-19 wt% Mg

C_L = 93 wt% Pb-7 wt% Mg

Inasmuch as the composition of the alloy C_0 = 85 wt% Pb and application of the appropriate lever rule expressions (for compositions in weight percent lead) leads to

$$W_{Mg_2Pb} = \frac{C_L - C_0}{C_L - C_{Mg_2Pb}} = \frac{93 - 85}{93 - 81} = 0.67$$

$$W_L = \frac{C_0 - C_{Mg_2Pb}}{C_L - C_{Mg_2Pb}} = \frac{85 - 81}{93 - 81} = 0.33$$

(g) From Problem 9.8g, just the α phase is present (i.e., W_α = 1.0) for an alloy composed of 8.2 mol Ni and 4.3 mol Cu (i.e., 63.8 wt% Ni-36.2 wt% Cu) at 1250°C; such may be noted (as point G) in the Cu-Ni phase diagram shown below.

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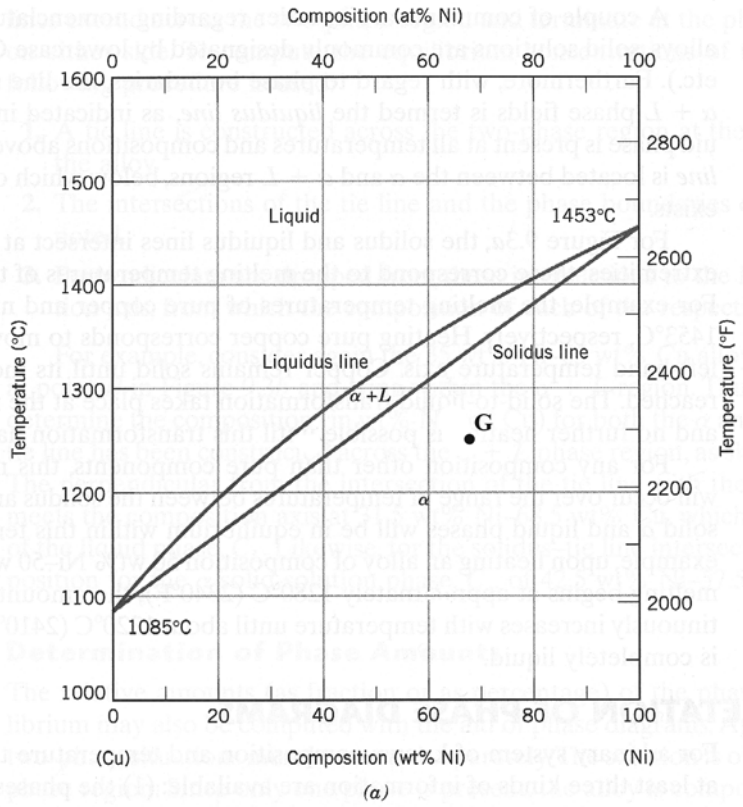
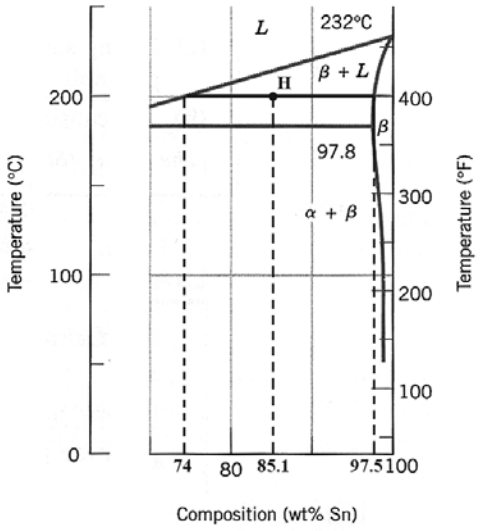


(h) From Problem 9.8h, β and *L* phases are present for an alloy composed of 4.5 mol Sn and 0.45 mol Pb (85.1 wt% Sn-14.9 wt% Pb) and at 200°C. This is represented in the portion of the Pb-Sn phase diagram shown below (at point H).



Furthermore, the compositions of the phases, as determined from the tie line are

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C_β = 97.5 wt% Sn-2.5 wt% Pb

C_L = 74 wt% Sn-26 wt% Pb

Inasmuch as the composition of the alloy C_0 = 85.1 wt% Sn, application of the appropriate lever rule expressions (for compositions in weight percent lead) leads to

$$W_\beta = \frac{C_0 - C_L}{C_\beta - C_L} = \frac{85.1 - 74}{97.5 - 74} = 0.47$$

$$W_L = \frac{C_\beta - C_0}{C_\beta - C_L} = \frac{97.5 - 85.1}{97.5 - 74} = 0.53$$

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9.15 *A 1.5-kg specimen of a 90 wt% Pb–10 wt% Sn alloy is heated to 250°C (480°F); at this temperature it is entirely an α-phase solid solution (Figure 9.8). The alloy is to be melted to the extent that 50% of the specimen is liquid, the remainder being the α phase. This may be accomplished either by heating the alloy or changing its composition while holding the temperature constant.*

(a) To what temperature must the specimen be heated?

(b) How much tin must be added to the 1.5-kg specimen at 250°C to achieve this state?

Solution

(a) Probably the easiest way to solve this part of the problem is by trial and error--that is, on the Pb-Sn phase diagram (Figure 9.8), moving vertically at the given composition, through the $\alpha + L$ region until the tie-line lengths on both sides of the given composition are the same. This occurs at approximately 295°C (560°F).

(b) We can also produce a 50% liquid solution at 250°C, by adding Sn to the alloy. At 250°C and within the $\alpha + L$ phase region

$$C_\alpha = 14 \text{ wt\% Sn-86 wt\% Pb}$$
$$C_L = 34 \text{ wt\% Sn-66 wt\% Pb}$$

Let C_0 be the new alloy composition to give $W_\alpha = W_L = 0.5$. Then,

$$W_\alpha = 0.5 = \frac{C_L - C_0}{C_L - C_\alpha} = \frac{34 - C_0}{34 - 14}$$

And solving for C_0 gives 24 wt% Sn. Now, let m_{Sn} be the mass of Sn added to the alloy to achieve this new composition. The amount of Sn in the original alloy is

$$(0.10)(1.5 \text{ kg}) = 0.15 \text{ kg}$$

Then, using a modified form of Equation 4.3

$$\left[\frac{0.15 \text{ kg} + m_{Sn}}{1.5 \text{ kg} + m_{Sn}}\right] \times 100 = 24$$

And, solving for m_{Sn} (the mass of tin to be added), yields $m_{Sn} = 0.276$ kg.

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9.16 *A magnesium-lead alloy of mass 5.5 kg consists of a solid α phase that has a composition that is just slightly below the solubility limit at 200°C (390°F).*

(a) What mass of lead is in the alloy?

(b) If the alloy is heated to 350°C (660°F), how much more lead may be dissolved in the α phase without exceeding the solubility limit of this phase?

Solution

(a) This portion of the problem asks that we calculate, for a Pb-Mg alloy, the mass of lead in 5.5 kg of the solid α phase at 200°C just below the solubility limit. From Figure 9.20, the solubility limit for the α phase at 200°C corresponds to the position (composition) of the α-α + Mg_2Pb phase boundary at this temperature, which is about 5 wt% Pb. Therefore, the mass of Pb in the alloy is just (0.05)(5.5 kg) = 0.28 kg.

(b) At 350°C, the solubility limit of the α phase increases to approximately 25 wt% Pb. In order to determine the additional amount of Pb that may be added (m_{Pb}), we utilize a modified form of Equation 4.3 as

$$C_{Pb} = 25 \text{ wt\%} = \frac{0.28 \text{ kg} + m_{Pb}}{5.5 \text{ kg} + m_{Pb}} \times 100$$

Solving for m_{Pb} yields $m_{Pb} = 1.46$ kg.

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9.17 *A 90 wt% Ag-10 wt% Cu alloy is heated to a temperature within the β + liquid phase region. If the composition of the liquid phase is 85 wt% Ag, determine:*

(a) The temperature of the alloy

(b) The composition of the β phase

(c) The mass fractions of both phases

Solution

(a) In order to determine the temperature of a 90 wt% Ag-10 wt% Cu alloy for which β and liquid phases are present with the liquid phase of composition 85 wt% Ag, we need to construct a tie line across the β + *L* phase region of Figure 9.7 that intersects the liquidus line at 85 wt% Ag; this is possible at about 850°C.

(b) The composition of the β phase at this temperature is determined from the intersection of this same tie line with solidus line, which corresponds to about 95 wt% Ag.

(c) The mass fractions of the two phases are determined using the lever rule, Equations 9.1 and 9.2 with C_0 = 90 wt% Ag, C_L = 85 wt% Ag, and C_β = 95 wt% Ag, as

$$W_\beta = \frac{C_0 - C_L}{C_\beta - C_L} = \frac{90 - 85}{95 - 85} = 0.50$$

$$W_L = \frac{C_\beta - C_0}{C_\beta - C_L} = \frac{95 - 90}{95 - 85} = 0.50$$

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9.18 *A 30 wt% Sn-70 wt% Pb alloy is heated to a temperature within the α + liquid phase region. If the mass fraction of each phase is 0.5, estimate:*

(a) The temperature of the alloy

(b) The compositions of the two phases

Solution

(a) We are given that the mass fractions of α and liquid phases are both 0.5 for a 30 wt% Sn-70 wt% Pb alloy and asked to estimate the temperature of the alloy. Using the appropriate phase diagram, Figure 9.8, by trial and error with a ruler, a tie line within the $\alpha + L$ phase region that is divided in half for an alloy of this composition exists at about 230°C.

(b) We are now asked to determine the compositions of the two phases. This is accomplished by noting the intersections of this tie line with both the solidus and liquidus lines. From these intersections, C_α = 15 wt% Sn, and C_L = 43 wt% Sn.

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9.19 *For alloys of two hypothetical metals A and B, there exist an α, A-rich phase and a β, B-rich phase. From the mass fractions of both phases for two different alloys provided in the table below, (which are at the same temperature), determine the composition of the phase boundary (or solubility limit) for both α and β phases at this temperature.*

Alloy Composition	***Fraction α Phase***	***Fraction β Phase***
60 wt% A–40 wt% B	*0.57*	*0.43*
30 wt% A–70 wt% B	*0.14*	*0.86*

Solution

The problem is to solve for compositions at the phase boundaries for both α and β phases (i.e., C_α and C_β). We may set up two independent lever rule expressions, one for each composition, in terms of C_α and C_β as follows:

$$W_{\alpha 1} = 0.57 = \frac{C_\beta - C_{01}}{C_\beta - C_\alpha} = \frac{C_\beta - 60}{C_\beta - C_\alpha}$$

$$W_{\alpha 2} = 0.14 = \frac{C_\beta - C_{02}}{C_\beta - C_\alpha} = \frac{C_\beta - 30}{C_\beta - C_\alpha}$$

In these expressions, compositions are given in wt% of A. Solving for C_α and C_β from these equations, yield

$$C_\alpha = 90 \text{ (or 90 wt\% A-10 wt\% B)}$$

$$C_\beta = 20.2 \text{ (or 20.2 wt\% A-79.8 wt\% B)}$$

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9.20 *A hypothetical A–B alloy of composition 55 wt% B–45 wt% A at some temperature is found to consist of mass fractions of 0.5 for both α and β phases. If the composition of the β phase is 90 wt% B–10 wt% A, what is the composition of the α phase?*

Solution

For this problem, we are asked to determine the composition of the β phase given that

$$C_0 = 55 \text{ (or 55 wt\% B-45 wt\% A)}$$

$$C_\beta = 90 \text{ (or 90 wt\% B-10 wt\% A)}$$

$$W_\alpha = W_\beta = 0.5$$

If we set up the lever rule for W_α

$$W_\alpha = 0.5 = \frac{C_\beta - C_0}{C_\beta - C_\alpha} = \frac{90 - 55}{90 - C_\alpha}$$

And solving for C_α

$$C_\alpha = 20 \text{ (or 20 wt\% B-80 wt\% A)}$$

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9.21 *Is it possible to have a copper-silver alloy of composition 50 wt% Ag-50 wt% Cu, which, at equilibrium, consists of α and β phases having mass fractions $W_\alpha = 0.60$ and $W_\beta = 0.40$? If so, what will be the approximate temperature of the alloy? If such an alloy is not possible, explain why.*

Solution

It is *not possible* to have a Cu-Ag alloy of composition 50 wt% Ag-50 wt% Cu which consists of mass fractions $W_\alpha = 0.60$ and $W_\beta = 0.40$. Using the appropriate phase diagram, Figure 9.7, and, using Equations 9.1 and 9.2 let us determine W_α and W_β at just below the eutectic temperature and also at room temperature. At just below the eutectic, $C_\alpha = 8.0$ wt% Ag and $C_\beta = 91.2$ wt% Ag; thus,

$$W_\alpha = \frac{C_\beta - C_0}{C_\beta - C_\alpha} = \frac{91.2 - 50}{91.2 - 8} = 0.50$$

$$W_\beta = 1.00 - W_\alpha = 1.00 - 0.50 = 0.50$$

Furthermore, at room temperature, $C_\alpha = 0$ wt% Ag and $C_\beta = 100$ wt% Ag; employment of Equations 9.1 and 9.2 yields

$$W_\alpha = \frac{C_\beta - C_0}{C_\beta - C_\alpha} = \frac{100 - 50}{100 - 0} = 0.50$$

And, $W_\beta = 0.50$. Thus, the mass fractions of the α and β phases, upon cooling through the α + β phase region will remain approximately constant at about 0.5, and will never have values of $W_\alpha = 0.60$ and $W_\beta = 0.40$ as called for in the problem.

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9.22 *For 11.20 kg of a magnesium-lead alloy of composition 30 wt% Pb-70 wt% Mg, is it possible, at equilibrium, to have α and Mg_2Pb phases having respective masses of 7.39 kg and 3.81 kg? If so, what will be the approximate temperature of the alloy? If such an alloy is not possible, explain why.*

Solution

Yes, it *is possible* to have a 30 wt% Pb-70 wt% Mg alloy which has masses of 7.39 kg and 3.81 kg for the α and Mg_2Pb phases, respectively. In order to demonstrate this, it is first necessary to determine the mass fraction of each phase as follows:

$$W_\alpha = \frac{m_\alpha}{m_\alpha + m_{Mg_2Pb}} = \frac{7.39\ \text{kg}}{7.39\ \text{kg} + 3.81\ \text{kg}} = 0.66$$

$$W_{Mg_2Pb} = 1.00 - 0.66 = 0.34$$

Now, if we apply the lever rule expression for W_α

$$W_\alpha = \frac{C_{Mg_2Pb} - C_0}{C_{Mg_2Pb} - C_\alpha}$$

Since the Mg_2Pb phase exists only at 81 wt% Pb, and C_0 = 30 wt% Pb

$$W_\alpha = 0.66 = \frac{81 - 30}{81 - C_\alpha}$$

Solving for C_α from this expression yields C_α = 3.7 wt% Pb. The position along the α–(α + Mg_2Pb) phase boundary of Figure 9.20 corresponding to this composition is approximately 190°C.

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9.23 *Derive Equations 9.6a and 9.7a, which may be used to convert mass fraction to volume fraction, and vice versa.*

Solution

This portion of the problem asks that we derive Equation 9.6a, which is used to convert from phase weight fraction to phase volume fraction. Volume fraction of phase α, V_α, is defined by Equation 9.5 as

$$V_\alpha = \frac{v_\alpha}{v_\alpha + v_\beta} \tag{9.S1}$$

where v_α and v_β are the volumes of the respective phases in the alloy. Furthermore, the density of each phase is equal to the ratio of its mass and volume, or upon rearrangement

$$v_\alpha = \frac{m_\alpha}{\rho_\alpha} \tag{9.S2a}$$

$$v_\beta = \frac{m_\beta}{\rho_\beta} \tag{9.S2b}$$

Substitution of these expressions into Equation 9.S1 leads to

$$V_\alpha = \frac{\dfrac{m_\alpha}{\rho_\alpha}}{\dfrac{m_\alpha}{\rho_\alpha} + \dfrac{m_\beta}{\rho_\beta}} \tag{9.S3}$$

in which m's and ρ's denote masses and densities, respectively. Now, the mass fractions of the α and β phases (i.e., W_α and W_β) are defined in terms of the phase masses as

$$W_\alpha = \frac{m_\alpha}{m_\alpha + m_\beta} \tag{9.S4a}$$

$$W_\beta = \frac{m_\beta}{m_\alpha + m_\beta} \tag{9.S4b}$$

Which, upon rearrangement yield

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$$m_\alpha = W_\alpha \left(m_\alpha + m_\beta \right) \tag{9.S5a}$$

$$m_\beta = W_\beta \left(m_\alpha + m_\beta \right) \tag{9.S5b}$$

Incorporation of these relationships into Equation 9.S3 leads to

$$V_\alpha = \frac{\dfrac{W_\alpha \left(m_\alpha + m_\beta \right)}{\rho_\alpha}}{\dfrac{W_\alpha \left(m_\alpha + m_\beta \right)}{\rho_\alpha} + \dfrac{W_\beta \left(m_\alpha + m_\beta \right)}{\rho_\beta}}$$

$$V_\alpha = \frac{\dfrac{W_\alpha}{\rho_\alpha}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_\beta}{\rho_\beta}} \tag{9.S6}$$

which is the desired equation.

For this portion of the problem we are asked to derive Equation 9.7a, which is used to convert from phase volume fraction to mass fraction. Mass fraction of the α phase is defined as

$$W_\alpha = \frac{m_\alpha}{m_\alpha + m_\beta} \tag{9.S7}$$

From Equations 9.S2a and 9.S2b

$$m_\alpha = v_\alpha \rho_\alpha \tag{9.S8a}$$

$$m_\beta = v_\beta \rho_\beta \tag{9.S8b}$$

Substitution of these expressions into Equation 9.S7 yields

$$W_\alpha = \frac{v_\alpha \rho_\alpha}{v_\alpha \rho_\alpha + v_\beta \rho_\beta} \tag{9.S9}$$

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From Equation 9.5 and its equivalent for V_β the following may be written:

$$v_\alpha = V_\alpha(v_\alpha + v_\beta) \tag{9.S10a}$$

$$v_\beta = V_\beta(v_\alpha + v_\beta) \tag{9.S10b}$$

Substitution of Equations 9.S10a and 9.S10b into Equation 9.S9 yields

$$W_\alpha = \frac{V_\alpha(v_\alpha + v_\beta)\rho_\alpha}{V_\alpha(v_\alpha + v_\beta)\rho_\alpha + V_\beta(v_\alpha + v_\beta)\rho_\beta}$$

$$W_\alpha = \frac{V_\alpha\rho_\alpha}{V_\alpha\rho_\alpha + V_\beta\rho_\beta} \tag{9.S11}$$

which is the desired expression.

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9.24 *Determine the relative amounts (in terms of volume fractions) of the phases for the alloys and temperatures given in Problem 9.8a, b, and c. Below are given the approximate densities of the various metals at the alloy temperatures:*

Metal	***Temperature (°C)***	***Density (g/cm^3)***
Ag	*900*	*9.97*
Cu	*400*	*8.77*
Cu	*900*	*8.56*
Pb	*175*	*11.20*
Sn	*175*	*7.22*
Zn	*400*	*6.83*

Solution

This problem asks that we determine the phase volume fractions for the alloys and temperatures in Problems 9.8a, b, and c. This is accomplished by using the technique illustrated in Example Problem 9.3, and also the results of Problems 9.8 and 9.14.

(a) This is a Cu-Zn alloy at 400°C, wherein

C_ε = 87 wt% Zn-13 wt% Cu
C_η = 97 wt% Zn-3 wt% Cu
W_ε = 0.70
W_η = 0.30
ρ_{Cu} = 8.77 g/cm^3
ρ_{Zn} = 6.83 g/cm^3

Using these data it is first necessary to compute the densities of the ε and η phases using Equation 4.10a. Thus

$$\rho_\varepsilon = \frac{100}{\frac{C_{Zn(\varepsilon)}}{\rho_{Zn}} + \frac{C_{Cu(\varepsilon)}}{\rho_{Cu}}}$$

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$$= \frac{100}{\frac{87}{6.83\ \text{g/cm}^3} + \frac{13}{8.77\ \text{g/cm}^3}} = 7.03\ \text{g/cm}^3$$

$$\rho_\eta = \frac{100}{\frac{C_{Zn(\eta)}}{\rho_{Zn}} + \frac{C_{Cu(\eta)}}{\rho_{Cu}}}$$

$$= \frac{100}{\frac{97}{6.83\ \text{g/cm}^3} + \frac{3}{8.77\ \text{g/cm}^3}} = 6.88\ \text{g/cm}^3$$

Now we may determine the V_ε and V_η values using Equation 9.6. Thus,

$$V_\varepsilon = \frac{\frac{W_\varepsilon}{\rho_\varepsilon}}{\frac{W_\varepsilon}{\rho_\varepsilon} + \frac{W_\eta}{\rho_\eta}}$$

$$= \frac{\frac{0.70}{7.03\ \text{g/cm}^3}}{\frac{0.70}{7.03\ \text{g/cm}^3} + \frac{0.30}{6.88\ \text{g/cm}^3}} = 0.70$$

$$V_\eta = \frac{\frac{W_\eta}{\rho_\eta}}{\frac{W_\varepsilon}{\rho_\varepsilon} + \frac{W_\eta}{\rho_\eta}}$$

$$= \frac{\frac{0.30}{6.88\ \text{g/cm}^3}}{\frac{0.70}{7.03\ \text{g/cm}^3} + \frac{0.30}{6.88\ \text{g/cm}^3}} = 0.30$$

(b) This is a Pb-Sn alloy at 175°C, wherein

C_α = 16 wt% Sn-84 wt% Pb

C_β = 97 wt% Sn-3 wt% Pb

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$W_\alpha = 0.27$

$W_\beta = 0.73$

$\rho_{Sn} = 7.22\ g/cm^3$

$\rho_{Pb} = 11.20\ g/cm^3$

Using this data it is first necessary to compute the densities of the α and β phases. Thus

$$\rho_\alpha = \frac{100}{\frac{C_{Sn(\alpha)}}{\rho_{Sn}} + \frac{C_{Pb(\alpha)}}{\rho_{Pb}}}$$

$$= \frac{100}{\frac{16}{7.22\ g/cm^3} + \frac{84}{11.20\ g/cm^3}} = 10.29\ g/cm^3$$

$$\rho_\beta = \frac{100}{\frac{C_{Sn(\beta)}}{\rho_{Sn}} + \frac{C_{Pb(\beta)}}{\rho_{Pb}}}$$

$$= \frac{100}{\frac{97}{7.22\ g/cm^3} + \frac{3}{11.20\ g/cm^3}} = 7.30\ g/cm^3$$

Now we may determine the V_α and V_β values using Equation 9.6. Thus,

$$V_\alpha = \frac{\frac{W_\alpha}{\rho_\alpha}}{\frac{W_\alpha}{\rho_\alpha} + \frac{W_\beta}{\rho_\beta}}$$

$$= \frac{\frac{0.27}{10.29\ g/cm^3}}{\frac{0.27}{10.29\ g/cm^3} + \frac{0.73}{7.30\ g/cm^3}} = 0.21$$

$$V_\beta = \frac{\frac{W_\beta}{\rho_\beta}}{\frac{W_\alpha}{\rho_\alpha} + \frac{W_\beta}{\rho_\beta}}$$

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$$= \frac{\dfrac{0.73}{7.30\ \text{g/cm}^3}}{\dfrac{0.27}{10.29\ \text{g/cm}^3} + \dfrac{0.73}{7.30\ \text{g/cm}^3}} = 0.79$$

(c) This is a Ag-Cu alloy at 900°C, wherein only the liquid phase is present. Therefore, $V_L = 1.0$.

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Development of Microstructure in Isomorphous Alloys

9.25 *(a) Briefly describe the phenomenon of coring and why it occurs.*

(b) Cite one undesirable consequence of coring.

Solution

(a) Coring is the phenomenon whereby concentration gradients exist across grains in polycrystalline alloys, with higher concentrations of the component having the lower melting temperature at the grain boundaries. It occurs, during solidification, as a consequence of cooling rates that are too rapid to allow for the maintenance of the equilibrium composition of the solid phase.

(b) One undesirable consequence of a cored structure is that, upon heating, the grain boundary regions will melt first and at a temperature below the equilibrium phase boundary from the phase diagram; this melting results in a loss in mechanical integrity of the alloy.

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Mechanical Properties of Isomorphous Alloys

9.26 *It is desirable to produce a copper-nickel alloy that has a minimum noncold-worked tensile strength of 350 MPa (50,750 psi) and a ductility of at least 48%EL. Is such an alloy possible? If so, what must be its composition? If this is not possible, then explain why.*

Solution

From Figure 9.6*a*, a tensile strength greater than 350 MPa (50,750 psi) is possible for compositions between about 22.5 and 98 wt% Ni. On the other hand, according to Figure 9.6*b*, ductilities greater than 48%EL exist for compositions less than about 8 wt% and greater than about 98 wt% Ni. Therefore, the stipulated criteria are met only at a composition of 98 wt% Ni.

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Binary Eutectic Systems

9.27 *A 45 wt% Pb–55 wt% Mg alloy is rapidly quenched to room temperature from an elevated temperature in such a way that the high-temperature microstructure is preserved. This microstructure is found to consist of the α phase and Mg_2Pb, having respective mass fractions of 0.65 and 0.35. Determine the approximate temperature from which the alloy was quenched.*

Solution

We are asked to determine the approximate temperature from which a 45 wt% Pb-55 wt% Mg alloy was quenched, given the mass fractions of α and Mg_2Pb phases. We can write a lever-rule expression for the mass fraction of the α phase as

$$W_\alpha = 0.65 = \frac{C_{Mg_2Pb} - C_0}{C_{Mg_2Pb} - C_\alpha}$$

The value of C_0 is stated as 45 wt% Pb-55 wt% Mg, and C_{Mg_2Pb} is 81 wt% Pb-19 wt% Mg, which is independent of temperature (Figure 9.20); thus,

$$0.65 = \frac{81 - 45}{81 - C_\alpha}$$

which yields

$$C_\alpha = 25.6 \text{ wt\% Pb}$$

The temperature at which the α–(α + Mg_2Pb) phase boundary (Figure 9.20) has a value of 25.6 wt% Pb is about 360°C (680°F).

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Development of Microstructure in Eutectic Alloys

9.28 *Briefly explain why, upon solidification, an alloy of eutectic composition forms a microstructure consisting of alternating layers of the two solid phases.*

Solution

Upon solidification, an alloy of eutectic composition forms a microstructure consisting of alternating layers of the two solid phases because during the solidification atomic diffusion must occur, and with this layered configuration the diffusion path length for the atoms is a minimum.

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9.29 *What is the difference between a phase and a microconstituent?*

Solution

A “phase” is a homogeneous portion of the system having uniform physical and chemical characteristics, whereas a “microconstituent” is an identifiable element of the microstructure (that may consist of more than one phase).

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9.30 *Is it possible to have a copper-silver alloy in which the mass fractions of primary β and total β are 0.68 and 0.925, respectively, at 775°C (1425°F)? Why or why not?*

Solution

This problem asks if it is possible to have a Cu-Ag alloy for which the mass fractions of primary β and total β are 0.68 and 0.925, respectively at 775°C. In order to make this determination we need to set up the appropriate lever rule expression for each of these quantities. From Figure 9.7 and at 775°C, C_α = 8.0 wt% Ag, C_β = 91.2 wt% Ag, and $C_{eutectic}$ = 71.9 wt% Ag.

For primary β

$$W_{\beta'} = \frac{C_0 - C_{eutectic}}{C_\beta - C_{eutectic}} = \frac{C_0 - 71.9}{91.2 - 71.9} = 0.68$$

Solving for C_0 gives C_0 = 85 wt% Ag.

Now the analogous expression for total β

$$W_\beta = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha} = \frac{C_0 - 8.0}{91.2 - 8.0} = 0.925$$

And this value of C_0 is 85 wt% Ag. Therefore, since these two C_0 values are the same (85 wt% Ag), this alloy *is possible*.

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9.31 *For 6.70 kg of a magnesium-lead alloy, is it possible to have the masses of primary α and total α of 4.23 kg and 6.00 kg, respectively, at 460°C (860°F)? Why or why not?*

Solution

This problem asks if it is possible to have a Mg-Pb alloy for which the masses of primary α and total α are 4.23 kg and 6.00 kg, respectively in 6.70 kg total of the alloy at 460°C. In order to make this determination we first need to convert these masses to mass fractions. Thus,

$$W_{\alpha'} = \frac{4.23\ \text{kg}}{6.70\ \text{kg}} = 0.631$$

$$W_{\alpha} = \frac{6.00\ \text{kg}}{6.70\ \text{kg}} = 0.896$$

Next it is necessary to set up the appropriate lever rule expression for each of these quantities. From Figure 9.20 and at 460°C, $C_{\alpha} = 41$ wt% Pb, $C_{Mg_2Pb} = 81$ wt% Pb, and $C_{\text{eutectic}} = 66$ wt% Pb

For primary α

$$W_{\alpha'} = \frac{C_{\text{eutectic}} - C_0}{C_{\text{eutectic}} - C_{\alpha}} = \frac{66 - C_0}{66 - 41} = 0.631$$

And solving for C_0 gives $C_0 = 50.2$ wt% Pb.

Now the analogous expression for total α

$$W_{\alpha} = \frac{C_{Mg_2Pb} - C_0}{C_{Mg_2Pb} - C_{\alpha}} = \frac{81 - C_0}{81 - 41} = 0.896$$

And this value of C_0 is 45.2 wt% Pb. Therefore, since these two C_0 values are different, this alloy is *not possible*.

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9.32 *For a copper-silver alloy of composition 25 wt% Ag-75 wt% Cu and at 775°C (1425°F) do the following:*

(a) Determine the mass fractions of α and β phases.

(b) Determine the mass fractions of primary α and eutectic microconstituents.

(c) Determine the mass fraction of eutectic α.

Solution

(a) This portion of the problem asks that we determine the mass fractions of α and β phases for an 25 wt% Ag-75 wt% Cu alloy (at 775°C). In order to do this it is necessary to employ the lever rule using a tie line that extends entirely across the α + β phase field. From Figure 9.7 and at 775°C, C_α = 8.0 wt% Ag, C_β = 91.2 wt% Ag, and C_{eutectic} = 71.9 wt% Sn. Therefore, the two lever-rule expressions are as follows:

$$W_\alpha = \frac{C_\beta - C_0}{C_\beta - C_\alpha} = \frac{91.2 - 25}{91.2 - 8.0} = 0.796$$

$$W_\beta = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha} = \frac{25 - 8.0}{91.2 - 8.0} = 0.204$$

(b) Now it is necessary to determine the mass fractions of primary α and eutectic microconstituents for this same alloy. This requires us to utilize the lever rule and a tie line that extends from the maximum solubility of Ag in the α phase at 775°C (i.e., 8.0 wt% Ag) to the eutectic composition (71.9 wt% Ag). Thus

$$W_{\alpha'} = \frac{C_{\text{eutectic}} - C_0}{C_{\text{eutectic}} - C_\alpha} = \frac{71.9 - 25}{71.9 - 8.0} = 0.734$$

$$W_e = \frac{C_0 - C_\alpha}{C_{\text{eutectic}} - C_\alpha} = \frac{25 - 8.0}{71.9 - 8.0} = 0.266$$

(c) And, finally, we are asked to compute the mass fraction of eutectic α, $W_{e\alpha}$. This quantity is simply the difference between the mass fractions of total α and primary α as

$$W_{e\alpha} = W_\alpha - W_{\alpha'} = 0.796 - 0.734 = 0.062$$

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9.33 *The microstructure of a lead-tin alloy at 180°C (355°F) consists of primary β and eutectic structures. If the mass fractions of these two microconstituents are 0.57 and 0.43, respectively, determine the composition of the alloy.*

Solution

Since there is a primary β microconstituent present, then we know that the alloy composition, C_0 is between 61.9 and 97.8 wt% Sn (Figure 9.8). Furthermore, this figure also indicates that C_β = 97.8 wt% Sn and C_{eutectic} = 61.9 wt% Sn. Applying the appropriate lever rule expression for $W_{\beta'}$

$$W_{\beta'} = \frac{C_0 - C_{\text{eutectic}}}{C_\beta - C_{\text{eutectic}}} = \frac{C_0 - 61.9}{97.8 - 61.9} = 0.57$$

and solving for C_0 yields C_0 = 82.4 wt% Sn.

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9.34 *Consider the hypothetical eutectic phase diagram for metals A and B, which is similar to that for the lead-tin system, Figure 9.8. Assume that (1) α and β phases exist at the A and B extremities of the phase diagram, respectively; (2) the eutectic composition is 47 wt% B-53 wt% A; and (3) the composition of the β phase at the eutectic temperature is 92.6 wt% B-7.4 wt% A. Determine the composition of an alloy that will yield primary α and total α mass fractions of 0.356 and 0.693, respectively.*

Solution

We are given a hypothetical eutectic phase diagram for which $C_{\text{eutectic}} = 47$ wt% B, $C_{\beta} = 92.6$ wt% B at the eutectic temperature, and also that $W_{\alpha'} = 0.356$ and $W_{\alpha} = 0.693$; from this we are asked to determine the composition of the alloy. Let us write lever rule expressions for $W_{\alpha'}$ and W_{α}

$$W_{\alpha} = \frac{C_{\beta} - C_0}{C_{\beta} - C_{\alpha}} = \frac{92.6 - C_0}{92.6 - C_{\alpha}} = 0.693$$

$$W_{\alpha'} = \frac{C_{\text{eutectic}} - C_0}{C_{\text{eutectic}} - C_{\alpha}} = \frac{47 - C_0}{47 - C_{\alpha}} = 0.356$$

Thus, we have two simultaneous equations with C_0 and C_{α} as unknowns. Solving them for C_0 gives $C_0 = 32.6$ wt% B.

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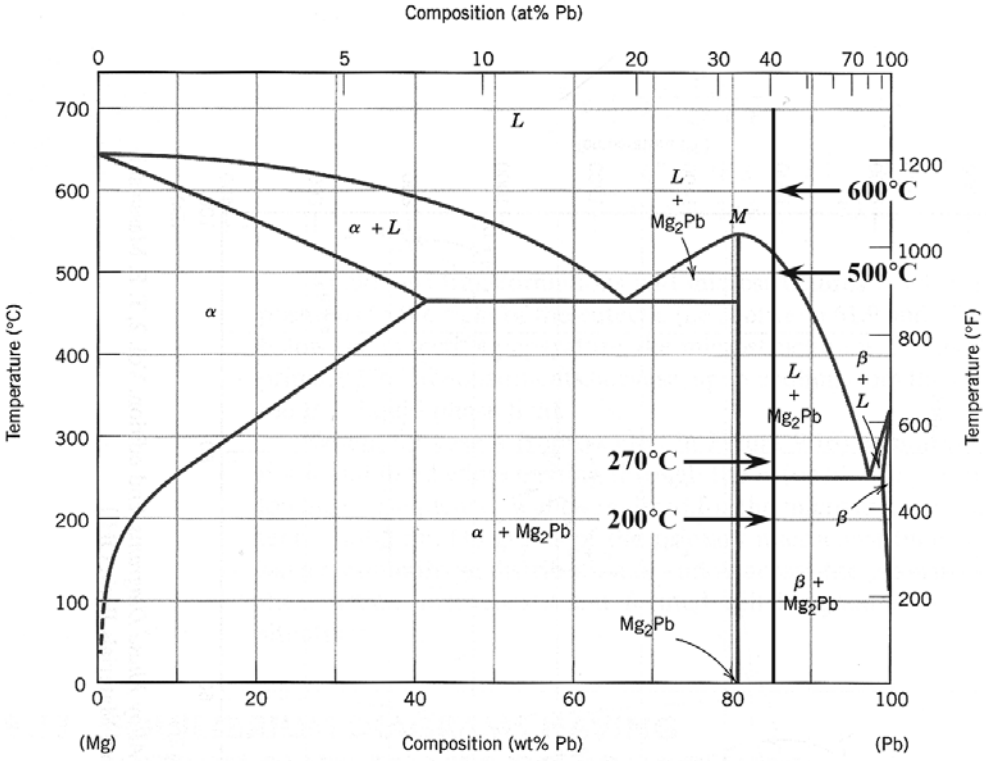
9.35 *For an 85 wt% Pb-15 wt% Mg alloy, make schematic sketches of the microstructure that would be observed for conditions of very slow cooling at the following temperatures: 600°C (1110°F), 500°C (930°F), 270°C (520°F), and 200°C (390°F). Label all phases and indicate their approximate compositions.*

Solution

The illustration below is the Mg-Pb phase diagram (Figure 9.20). A vertical line at a composition of 85 wt% Pb-15 wt% Mg has been drawn, and, in addition, horizontal arrows at the four temperatures called for in the problem statement (i.e., 600°C, 500°C, 270°C, and 200°C).



On the basis of the locations of the four temperature-composition points, schematic sketches of the four respective microstructures along with phase compositions are represented as follows:

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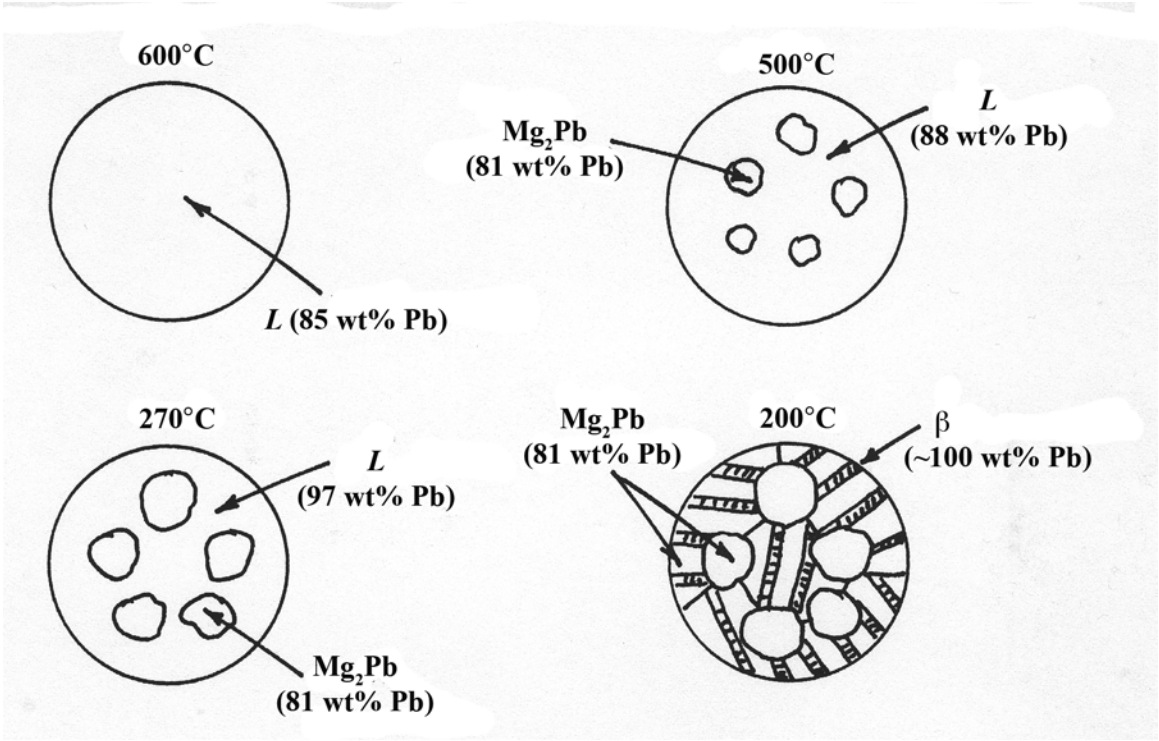

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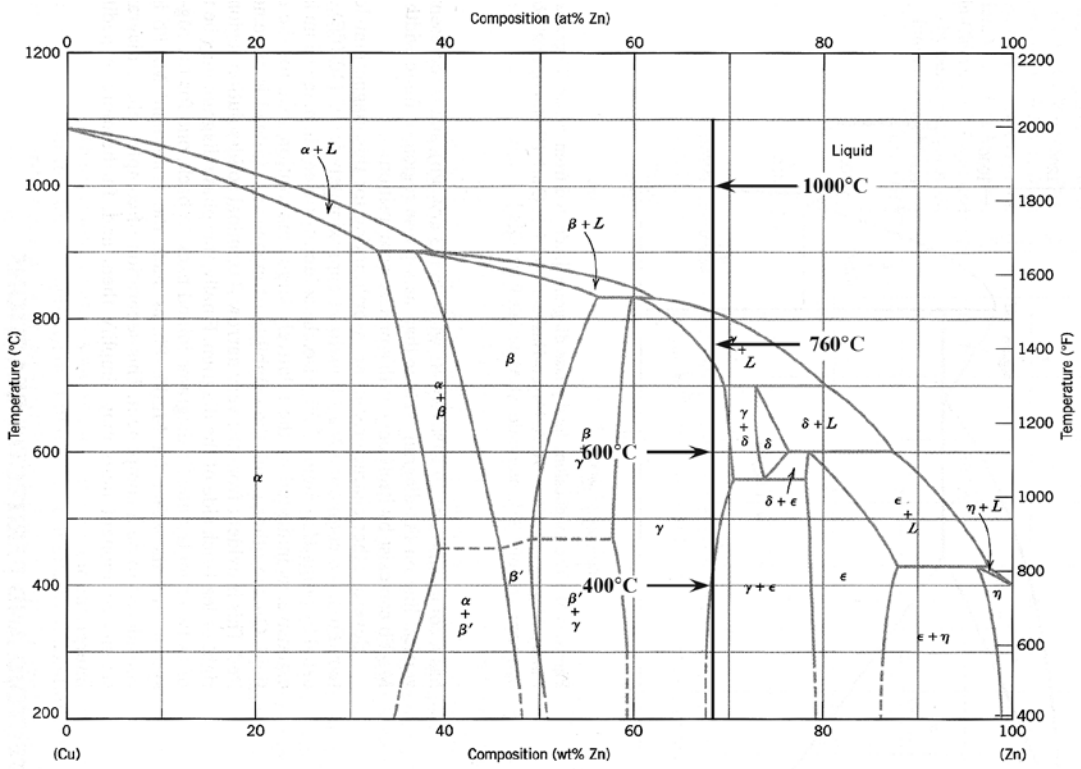
9.36 *For a 68 wt% Zn-32 wt% Cu alloy, make schematic sketches of the microstructure that would be observed for conditions of very slow cooling at the following temperatures: 1000°C (1830°F), 760°C (1400°F), 600°C (1110°F), and 400°C (750°F). Label all phases and indicate their approximate compositions.*

Solution

The illustration below is the Cu-Zn phase diagram (Figure 9.19). A vertical line at a composition of 68 wt% Zn-32 wt% Cu has been drawn, and, in addition, horizontal arrows at the four temperatures called for in the problem statement (i.e., 1000°C, 760°C, 600°C, and 400°C).



On the basis of the locations of the four temperature-composition points, schematic sketches of the four respective microstructures along with phase compositions are represented as follows:

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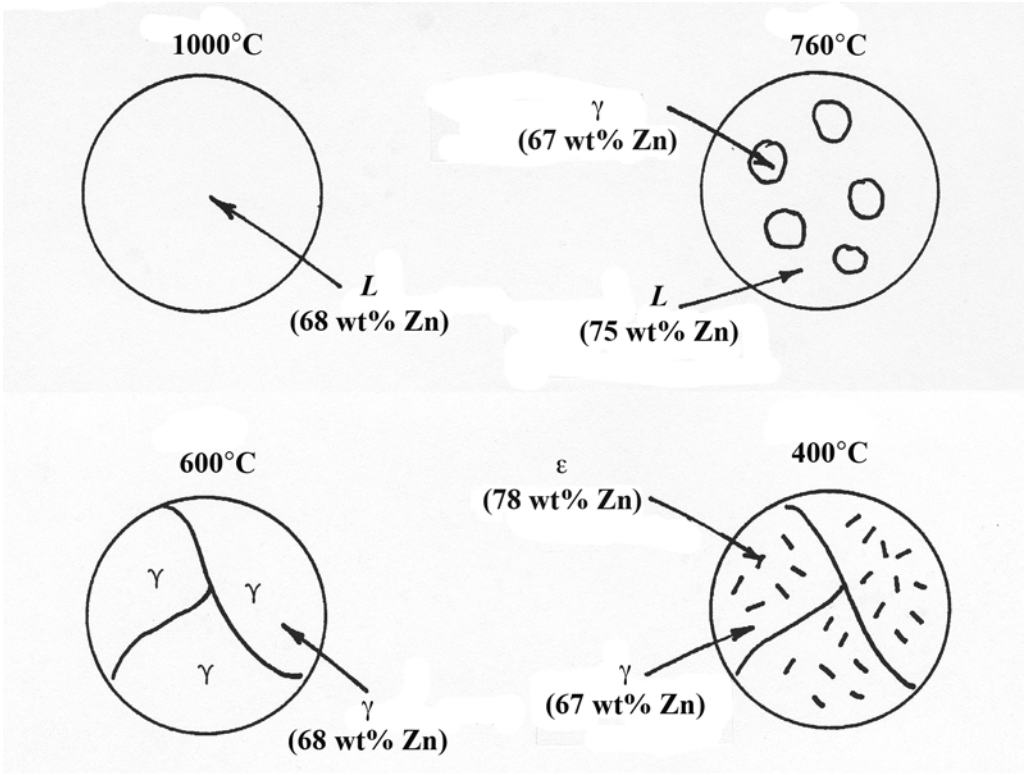

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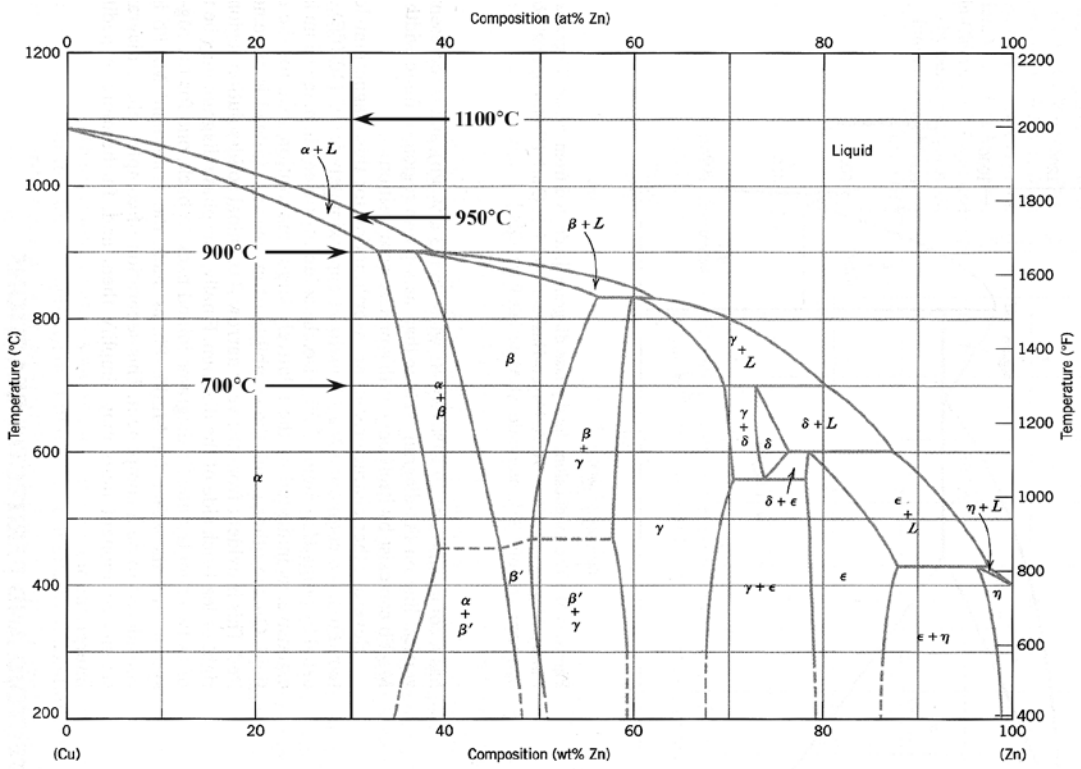
9.37 *For a 30 wt% Zn-70 wt% Cu alloy, make schematic sketches of the microstructure that would be observed for conditions of very slow cooling at the following temperatures: 1100°C (2010°F), 950°C (1740°F), 900°C (1650°F), and 700°C (1290°F). Label all phases and indicate their approximate compositions.*

Solution

The illustration below is the Cu-Zn phase diagram (Figure 9.19). A vertical line at a composition of 30 wt% Zn-70 wt% Cu has been drawn, and, in addition, horizontal arrows at the four temperatures called for in the problem statement (i.e., 1100°C, 950°C, 900°C, and 700°C).



On the basis of the locations of the four temperature-composition points, schematic sketches of the four respective microstructures along with phase compositions are represented as follows:

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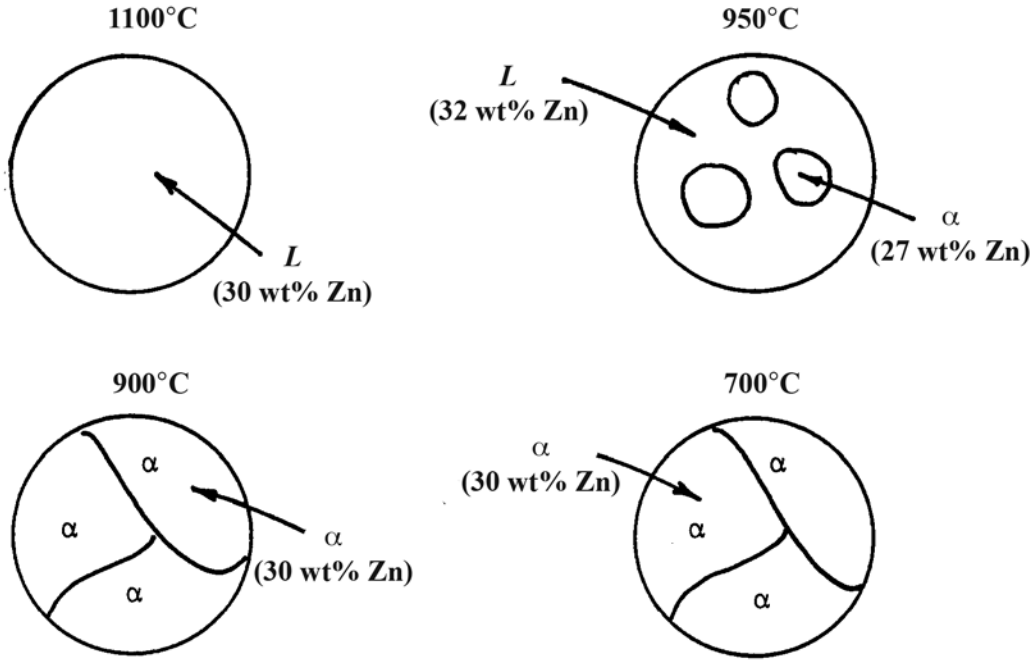

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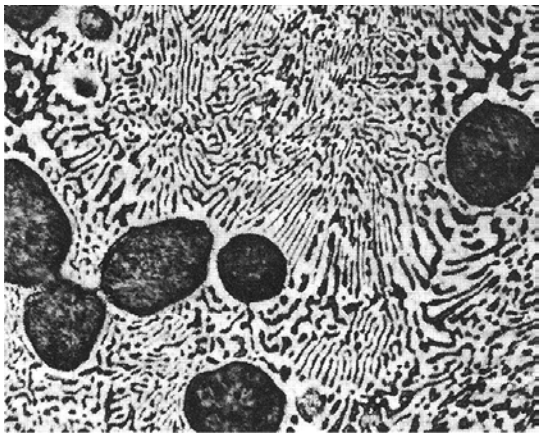
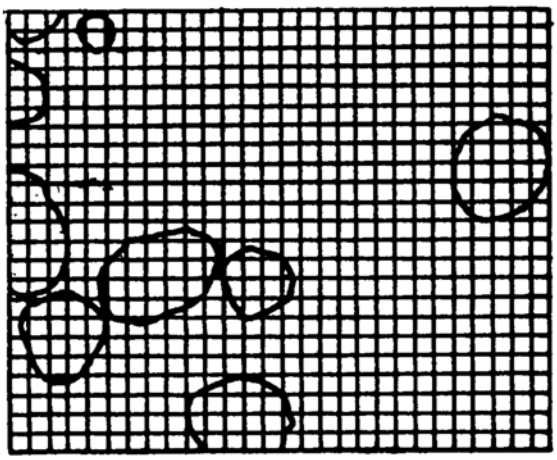
9.38 *On the basis of the photomicrograph (i.e., the relative amounts of the microconstituents) for the lead–tin alloy shown in Figure 9.17 and the Pb–Sn phase diagram (Figure 9.8), estimate the composition of the alloy, and then compare this estimate with the composition given in the figure legend of Figure 9.17. Make the following assumptions: (1) the area fraction of each phase and microconstituent in the photomicrograph is equal to its volume fraction; (2) the densities of the α and β phases as well as the eutectic structure are 11.2, 7.3, and 8.7 g/cm^3, respectively; and (3) this photomicrograph represents the equilibrium microstructure at 180°C (355°F).*

Solution

Below is shown the micrograph of the Pb-Sn alloy, Figure 9.17:



Primary α and eutectic microconstituents are present in the photomicrograph, and it is given that their densities are 11.2 and 8.7 g/cm^3, respectively. Below is shown a square grid network onto which is superimposed outlines of the primary α phase areas.



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The area fraction of this primary α phase may be determined by counting squares. There are a total of 644 squares, and of these, approximately 104 lie within the primary α phase particles. Thus, the area fraction of primary α is 104/644 = 0.16, which is also assumed to be the volume fraction.

We now want to convert the volume fractions into mass fractions in order to employ the lever rule to the Pb-Sn phase diagram. To do this, it is necessary to utilize Equations 9.7a and 9.7b as follows:

$$W_{\alpha'} = \frac{V_{\alpha'}\,\rho_{\alpha'}}{V_{\alpha'}\rho_{\alpha'} + V_{\text{eutectic}}\,\rho_{\text{eutectic}}}$$

$$= \frac{(0.16)(11.2\ \text{g/cm}^3)}{(0.16)(11.2\ \text{g/cm}^3) + (0.84)(8.7\ \text{g/cm}^3)} = 0.197$$

$$W_{\text{eutectic}} = \frac{V_{\text{eutectic}}\,\rho_{\text{eutectic}}}{V_{\alpha'}\rho_{\alpha'} + V_{\text{eutectic}}\,\rho_{\text{eutectic}}}$$

$$= \frac{(0.84)(8.7\ \text{g/cm}^3)}{(0.16)(11.2\ \text{g/cm}^3) + (0.84)(8.7\ \text{g/cm}^3)} = 0.803$$

From Figure 9.8, we want to use the lever rule and a tie-line that extends from the eutectic composition (61.9 wt% Sn) to the α–(α + β) phase boundary at 180°C (about 18.3 wt% Sn). Accordingly

$$W_{\alpha'} = 0.197 = \frac{61.9 - C_0}{61.9 - 18.3}$$

wherein C_0 is the alloy composition (in wt% Sn). Solving for C_0 yields C_0 = 53.3 wt% Sn. This value is in good agreement with the actual composition—viz. 50 wt% Sn.

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9.39 *The room-temperature tensile strengths of pure lead and pure tin are 16.8 MPa and 14.5 MPa, respectively.*

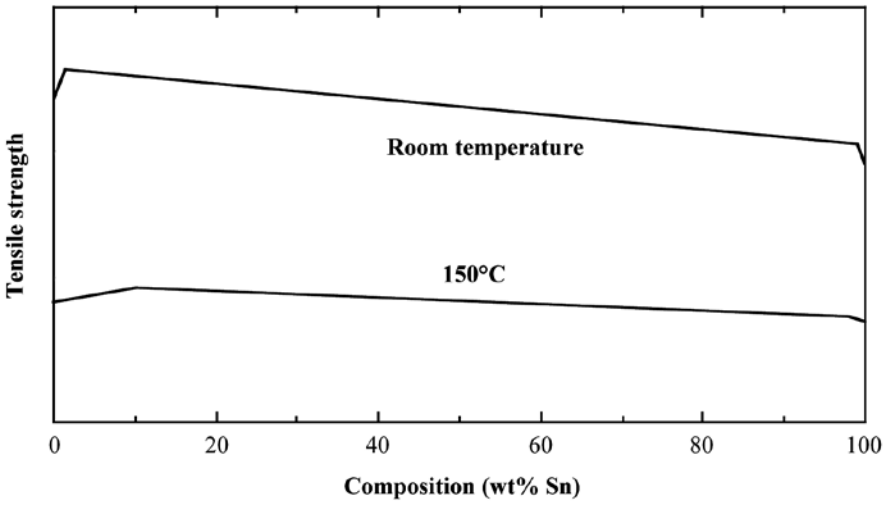
(a) Make a schematic graph of the room-temperature tensile strength versus composition for all compositions between pure lead and pure tin. (Hint: you may want to consult Sections 9.10 and 9.11, as well as Equation 9.24 in Problem 9.64.)

(b) On this same graph schematically plot tensile strength versus composition at 150°C.

(c) Explain the shapes of these two curves, as well as any differences between them.

Solution

The (a) and (b) portions of the problem ask that we make schematic plots on the same graph for the tensile strength versus composition for lead-tin alloys at both room temperature and 150°C; such a graph is shown below.



(c) Upon consultation of the Pb-Sn phase diagram (Figure 9.8) we note that, at room temperature (20°C), about 1.5 wt% of Sn is soluble in Pb (within the α-phase region at the left extremity of the phase diagram). Similarly, only about 1 wt% of Pb is soluble in Sn (within the β-phase region at the left extremity). Thus, there will a solid-solution strengthening effect on both ends of the phase diagram—strength increases slightly with additions of Sn to Pb [in the α phase region (left-hand side)] and with additions of Pb to Sn [in the β phase region (right-hand side)]; these effects are noted in the above figure. This figure also shows that the tensile strength of pure lead is greater than pure tin, which is in agreement with tensile strength values provided in the problem statement.

In addition, at room temperature, for compositions between about 1.5 wt% Sn and 99 wt% Sn, both α and β phase will coexist, (Figure 9.8), Furthermore, for compositions within this range, tensile strength will depend (approximately) on the tensile strengths of each of the α and β phases as well as their phase fractions in a manner described by Equation 9.24 for the elastic modulus (Problem 9.64). That is, for this problem

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$$(TS)_{\text{alloy}} \cong (TS)_{\alpha} V_{\alpha} + (TS)_{\beta} V_{\beta}$$

in which TS and V denote tensile strength and volume fraction, respectively, and the subscripts represent the alloy/phases. Also, mass fractions of the α and β phases change linearly with changing composition (according to the lever rule). Furthermore, although there is some disparity between the densities of Pb and Sn (11.35 versus 7.27 g/cm^3), weight and volume fractions of the α and β phases will also be similar (see Equation 9.6).

At 150°C, the curve will be shifted to significantly lower tensile strengths inasmuch as tensile strength diminishes with increasing temperature (Section 6.6, Figure 6.14). In addition, according to Figure 9.8, solubility limits for both α and β phases increase—for the α phase from 1.5 to 10 wt% Sn, and for the β phase from 1 to about 2 wt% Pb. Thus, the compositional ranges over which solid-solution strengthening occurs increase somewhat from the room-temperature ranges; these effects are also noted on the 150°C curve above. Furthermore, at 150°C, it would be expected that the tensile strength of lead will be greater than that of tin; and for compositions over which both α and β phases coexist, strength will decrease approximately linearly with increasing Sn content.

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Equilibrium Diagrams Having Intermediate Phases or Compounds

9.40 *Two intermetallic compounds, AB and AB_2, exist for elements A and B. If the compositions for AB and AB_2 are 34.3 wt% A–65.7 wt% B and 20.7 wt% A–79.3 wt% B, respectively, and element A is potassium, identify element B.*

Solution

This problem gives us the compositions in weight percent for the two intermetallic compounds AB and AB_2, and then asks us to identify element B if element A is potassium. Probably the easiest way to solve this problem is to first compute the ratio of the atomic weights of these two elements using Equation 4.6a; then, since we know the atomic weight of potassium (39.10 g/mol, per inside the front cover), it is possible to determine the atomic weight of element B, from which an identification may be made.

First of all, consider the AB intermetallic compound; inasmuch as it contains the same numbers of A and B atoms, its composition in atomic percent is 50 at% A-50 at% B. Equation 4.6a may be written in the form:

$$C'_{\mathrm{B}} = \frac{C_{\mathrm{B}} A_{\mathrm{A}}}{C_{\mathrm{A}} A_{\mathrm{B}} + C_{\mathrm{B}} A_{\mathrm{A}}} \times 100$$

where A_{A} and A_{B} are the atomic weights for elements A and B, and C_{A} and C_{B} are their compositions in weight percent. For this AB compound, and making the appropriate substitutions in the above equation leads to

$$50 \text{ at\% B} = \frac{(65.7 \text{ wt\% B})(A_{\mathrm{A}})}{(34.3 \text{ wt\% A})(A_{\mathrm{B}}) + (65.7 \text{ wt\% B})(A_{\mathrm{A}})} \times 100$$

Now, solving this expression yields,

$$A_{\mathrm{B}} = 1.916\, A_{\mathrm{A}}$$

Since potassium is element A and it has an atomic weight of 39.10 g/mol, the atomic weight of element B is just

$$A_{\mathrm{B}} = (1.916)(39.10 \text{ g/mol}) = 74.92 \text{ g/mol}$$

Upon consultation of the period table of the elements (Figure 2.6) we note the element that has an atomic weight closest to this value is arsenic (74.92 g/mol). Therefore, element B is arsenic, and the two intermetallic compounds are KAs and KAs_2.

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Congruent Phase Transformations
Eutectoid and Peritectic Reactions

9.41 *What is the principal difference between congruent and incongruent phase transformations?*

Solution

The principal difference between congruent and incongruent phase transformations is that for congruent no compositional changes occur with any of the phases that are involved in the transformation. For incongruent there will be compositional alterations of the phases.

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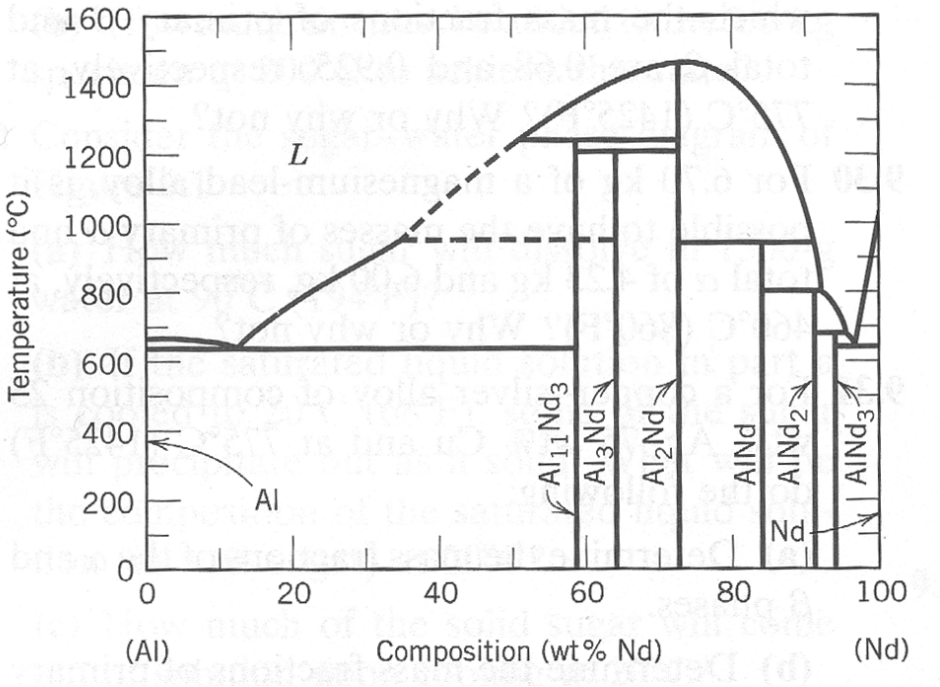
9.42 *Figure 9.36 is the aluminum-neodymium phase diagram, for which only single-phase regions are labeled. Specify temperature-composition points at which all eutectics, eutectoids, peritectics, and congruent phase transformations occur. Also, for each, write the reaction upon cooling.*

Solution

Below is shown the aluminum-neodymium phase diagram (Figure 9.36).



There are two eutectics on this phase diagram. One exists at 12 wt% Nd-88 wt% Al and 632°C. The reaction upon cooling is

$$L \rightarrow \text{Al} + \text{Al}_{11}\text{Nd}_3$$

The other eutectic exists at about 97 wt% Nd-3 wt% Al and 635°C. This reaction upon cooling is

$$L \rightarrow \text{AlNd}_3 + \text{Nd}$$

There are four peritectics. One exists at 59 wt% Nd-41 wt% Al and 1235°C. Its reaction upon cooling is as follows:

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$$L + Al_2Nd \rightarrow Al_{11}Nd_3$$

The second peritectic exists at 84 wt% Nd-16 wt% Al and 940°C. This reaction upon cooling is

$$L + Al_2Nd \rightarrow AlNd$$

The third peritectic exists at 91 wt% Nd-9 wt% Al and 795°C. This reaction upon cooling is

$$L + AlNd \rightarrow AlNd_2$$

The fourth peritectic exists at 94 wt% Nd-6 wt% Al and 675°C. This reaction upon cooling is

$$L + AlNd_2 \rightarrow AlNd_3$$

There is one congruent melting point at about 73 wt% Nd-27 wt% Al and 1460°C. Its reaction upon cooling is

$$L \rightarrow Al_2Nd$$

No eutectoids are present.

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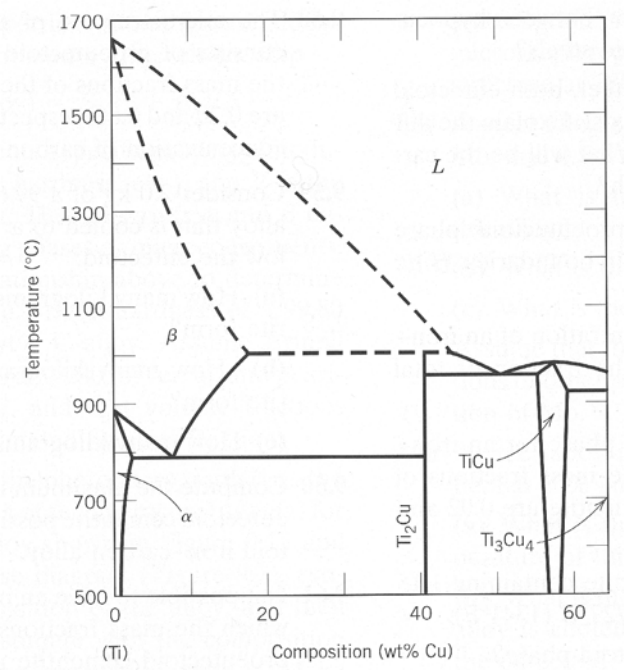
9.43 *Figure 9.37 is a portion of the titanium-copper phase diagram for which only single-phase regions are labeled. Specify all temperature-composition points at which eutectics, eutectoids, peritectics, and congruent phase transformations occur. Also, for each, write the reaction upon cooling.*

Solution

Below is shown the titanium-copper phase diagram (Figure 9.37).



There is one eutectic on this phase diagram, which exists at about 51 wt% Cu-49 wt% Ti and 960°C. Its reaction upon cooling is

$$L \rightarrow Ti_2Cu + TiCu$$

There is one eutectoid for this system. It exists at about 7.5 wt% Cu-92.5 wt% Ti and 790°C. This reaction upon cooling is

$$\beta \rightarrow \alpha + Ti_2Cu$$

There is one peritectic on this phase diagram. It exists at about 40 wt% Cu-60 wt% Ti and 1005°C. The reaction upon cooling is

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$$\beta + L \rightarrow Ti_2Cu$$

There is a single congruent melting point that exists at about 57.5 wt% Cu-42.5 wt% Ti and 982°C. The reaction upon cooling is

$$L \rightarrow TiCu$$

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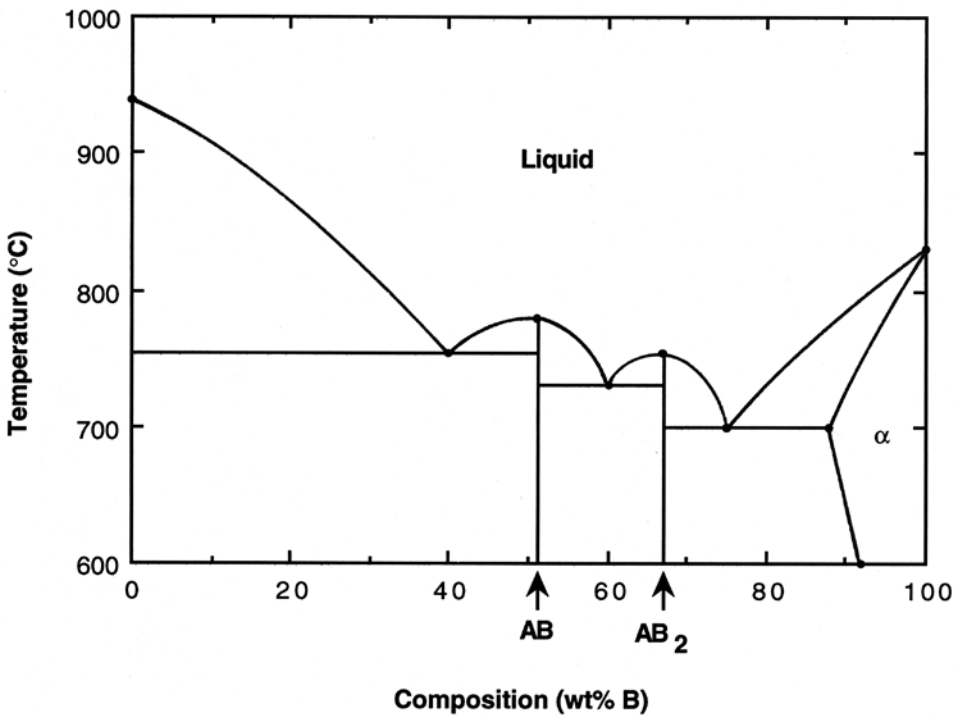
9.44 *Construct the hypothetical phase diagram for metals A and B between temperatures of 600°C and 1000°C given the following information:*

- *The melting temperature of metal A is 940°C.*
- *The solubility of B in A is negligible at all temperatures.*
- *The melting temperature of metal B is 830°C.*
- *The maximum solubility of A in B is 12 wt% A, which occurs at 700°C.*
- *At 600°C, the solubility of A in B is 8 wt% A.*
- *One eutectic occurs at 700°C and 75 wt% B–25 wt% A.*
- *A second eutectic occurs at 730°C and 60 wt% B–40 wt% A.*
- *A third eutectic occurs at 755°C and 40 wt% B–60 wt% A.*
- *One congruent melting point occurs at 780°C and 51 wt% B–49 wt% A.*
- *A second congruent melting point occurs at 755°C and 67 wt% B–33 wt% A.*
- *The intermetallic compound AB exists at 51 wt% B–49 wt% A.*
- *The intermetallic compound AB_2 exists at 67 wt% B–33 wt% A.*

Solution

Below is shown the phase diagram for these two A and B metals.



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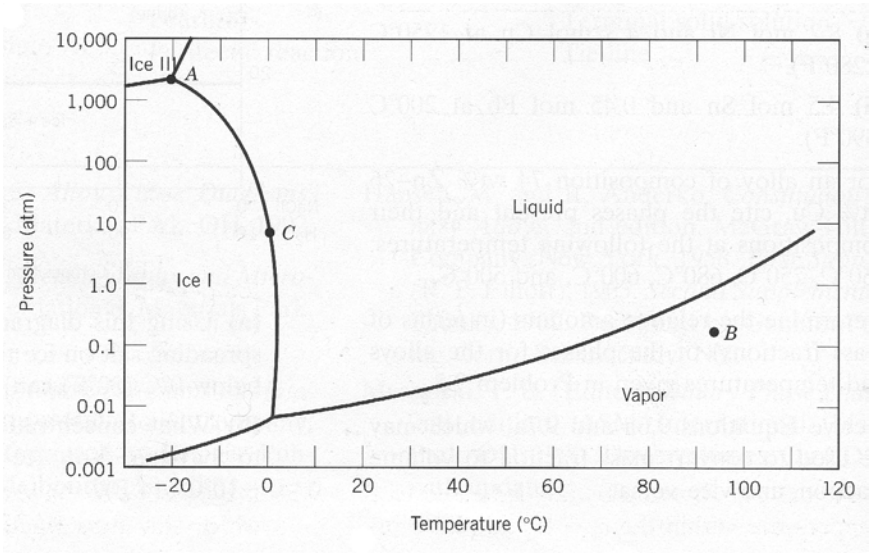
The Gibbs Phase Rule

9.45 *In Figure 9.38 is shown the pressure–temperature phase diagram for H_2O. Apply the Gibbs phase rule at points A, B, and C; that is, specify the number of degrees of freedom at each of the points—that is, the number of externally controllable variables that need be specified to completely define the system.*

Solution

We are asked to specify the value of F for Gibbs phase rule at points A, B, and C on the pressure-temperature diagram for H_2O, Figure 9.38, which is shown below.



Gibbs phase rule in general form is

$$P + F = C + N$$

For this system, the number of components, C, is 1, whereas N, the number of noncompositional variables, is 2--viz. temperature and pressure. Thus, the phase rule now becomes

$$P + F = 1 + 2 = 3$$

Or

$$F = 3 - P$$

where P is the number of phases present at equilibrium.

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At point A, three phases are present (viz. ice I, ice III, and liquid) and $P = 3$; thus, the number of degrees of freedom is zero since

$$F = 3 - P = 3 - 3 = 0$$

Thus, point A is an invariant point (in this case a triple point), and we have no choice in the selection of externally controllable variables in order to define the system.

At point B on the figure, only a single (vapor) phase is present (i.e., $P = 1$), or

$$F = 3 - P = 3 - 1 = 2$$

which means that specification of both temperature and pressure are necessary to define the system.

And, finally, at point C which is on the phase boundary between liquid and ice I phases, two phases are in equilibrium ($P = 2$); hence

$$F = 3 - P = 3 - 2 = 1$$

Or that we need to specify the value of either temperature or pressure, which determines the value of the other parameter (pressure or temperature).

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The Iron-Iron Carbide (Fe-Fe_3C) Phase Diagram

Development of Microstructure in Iron-Carbon Alloys

9.46 *Compute the mass fractions of α ferrite and cementite in pearlite.*

Solution

This problem asks that we compute the mass fractions of α ferrite and cementite in pearlite. The lever-rule expression for ferrite is

$$W_\alpha = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_\alpha}$$

and, since C_{Fe_3C} = 6.70 wt% C, C_0 = 0.76 wt% C, and C_α = 0.022 wt% C

$$W_\alpha = \frac{6.70 - 0.76}{6.70 - 0.022} = 0.89$$

Similarly, for cementite

$$W_{Fe_3C} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} = \frac{0.76 - 0.022}{6.70 - 0.022} = 0.11$$

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9.47 *(a) What is the distinction between hypoeutectoid and hypereutectoid steels?*

(b) In a hypoeutectoid steel, both eutectoid and proeutectoid ferrite exist. Explain the difference between them. What will be the carbon concentration in each?

Solution

(a) A "hypoeutectoid" steel has a carbon concentration less than the eutectoid; on the other hand, a "hypereutectoid" steel has a carbon content greater than the eutectoid.

(b) For a hypoeutectoid steel, the proeutectoid ferrite is a microconstituent that formed above the eutectoid temperature. The eutectoid ferrite is one of the constituents of pearlite that formed at a temperature below the eutectoid. The carbon concentration for both ferrites is 0.022 wt% C.

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9.48 *What is the carbon concentration of an iron–carbon alloy for which the fraction of total ferrite is 0.94?*

Solution

This problem asks that we compute the carbon concentration of an iron-carbon alloy for which the fraction of total ferrite is 0.94. Application of the lever rule (of the form of Equation 9.12) yields

$$W_{\alpha} = 0.94 = \frac{C_{Fe_3C} - C_0'}{C_{Fe_3C} - C_{\alpha}} = \frac{6.70 - C_0'}{6.70 - 0.022}$$

and solving for C_0'

$$C_0' = 0.42 \text{ wt\% C}$$

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9.49 *What is the proeutectoid phase for an iron–carbon alloy in which the mass fractions of total ferrite and total cementite are 0.92 and 0.08, respectively? Why?*

Solution

In this problem we are given values of W_α and W_{Fe_3C} (0.92 and 0.08, respectively) for an iron-carbon alloy and then are asked to specify the proeutectoid phase. Employment of the lever rule for total α leads to

$$W_\alpha = 0.92 = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_\alpha} = \frac{6.70 - C_0}{6.70 - 0.022}$$

Now, solving for C_0, the alloy composition, leads to C_0 = 0.56 wt% C. Therefore, the proeutectoid phase is α-ferrite since C_0 is less than 0.76 wt% C.

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9.50 *Consider 1.0 kg of austenite containing 1.15 wt% C, cooled to below 727°C (1341°F).*

(a) What is the proeutectoid phase?

(b) How many kilograms each of total ferrite and cementite form?

(c) How many kilograms each of pearlite and the proeutectoid phase form?

(d) Schematically sketch and label the resulting microstructure.

Solution

(a) The proeutectoid phase will be Fe_3C since 1.15 wt% C is greater than the eutectoid composition (0.76 wt% C).

(b) For this portion of the problem, we are asked to determine how much total ferrite and cementite form. Application of the appropriate lever rule expression yields

$$W_\alpha = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_\alpha} = \frac{6.70 - 1.15}{6.70 - 0.022} = 0.83$$

which, when multiplied by the total mass of the alloy (1.0 kg), gives 0.83 kg of total ferrite.

Similarly, for total cementite,

$$W_{Fe_3C} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} = \frac{1.15 - 0.022}{6.70 - 0.022} = 0.17$$

And the mass of total cementite that forms is (0.17)(1.0 kg) = 0.17 kg.

(c) Now we are asked to calculate how much pearlite and the proeutectoid phase (cementite) form. Applying Equation 9.22, in which C_1' = 1.15 wt% C

$$W_p = \frac{6.70 - C_1'}{6.70 - 0.76} = \frac{6.70 - 1.15}{6.70 - 0.76} = 0.93$$

which corresponds to a mass of 0.93 kg. Likewise, from Equation 9.23

$$W_{Fe_3C'} = \frac{C_1' - 0.76}{5.94} = \frac{1.15 - 0.76}{5.94} = 0.07$$

which is equivalent to 0.07 kg of the total 1.0 kg mass.

(d) Schematically, the microstructure would appear as:

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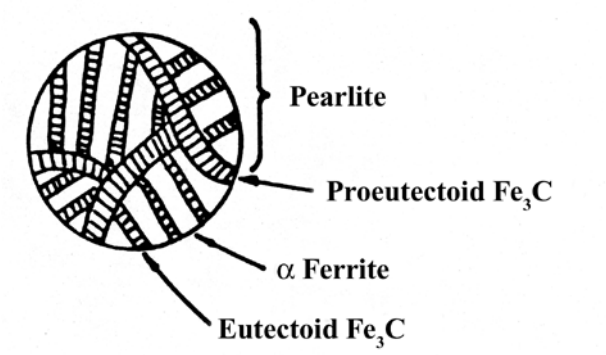

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9.51 *Consider 2.5 kg of austenite containing 0.65 wt% C, cooled to below 727°C (1341°F).*

(a) What is the proeutectoid phase?

(b) How many kilograms each of total ferrite and cementite form?

(c) How many kilograms each of pearlite and the proeutectoid phase form?

(d) Schematically sketch and label the resulting microstructure.

Solution

(a) Ferrite is the proeutectoid phase since 0.65 wt% C is less than 0.76 wt% C.

(b) For this portion of the problem, we are asked to determine how much total ferrite and cementite form. For ferrite, application of the appropriate lever rule expression yields

$$W_{\alpha} = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_{\alpha}} = \frac{6.70 - 0.65}{6.70 - 0.022} = 0.91$$

which corresponds to (0.91)(2.5 kg) = 2.27 kg of total ferrite.

Similarly, for total cementite,

$$W_{Fe_3C} = \frac{C_0 - C_{\alpha}}{C_{Fe_3C} - C_{\alpha}} = \frac{0.65 - 0.022}{6.70 - 0.022} = 0.09$$

Or (0.09)(2.5 kg) = 0.23 kg of total cementite form.

(c) Now consider the amounts of pearlite and proeutectoid ferrite. Using Equation 9.20

$$W_p = \frac{C'_0 - 0.022}{0.74} = \frac{0.65 - 0.022}{0.74} = 0.85$$

This corresponds to (0.85)(2.5 kg) = 2.12 kg of pearlite.

Also, from Equation 9.21,

$$W_{\alpha'} = \frac{0.76 - 0.65}{0.74} = 0.15$$

Or, there are (0.15)(2.5 kg) = 0.38 kg of proeutectoid ferrite.

(d) Schematically, the microstructure would appear as:

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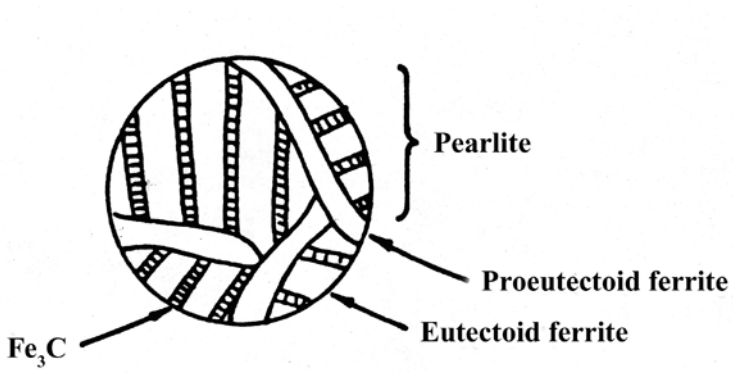

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9.52 *Compute the mass fractions of proeutectoid ferrite and pearlite that form in an iron–carbon alloy containing 0.25 wt% C.*

Solution

The mass fractions of proeutectoid ferrite and pearlite that form in a 0.25 wt% C iron-carbon alloy are considered in this problem. From Equation 9.20

$$W_p = \frac{C_0' - 0.022}{0.74} = \frac{0.25 - 0.022}{0.74} = 0.31$$

And, from Equation 9.21 (for proeutectoid ferrite)

$$W_{\alpha'} = \frac{0.76 - C_0'}{0.74} = \frac{0.76 - 0.25}{0.74} = 0.69$$

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9.53 *The microstructure of an iron–carbon alloy consists of proeutectoid ferrite and pearlite; the mass fractions of these two microconstituents are 0.286 and 0.714, respectively. Determine the concentration of carbon in this alloy.*

Solution

This problem asks that we determine the carbon concentration in an iron-carbon alloy, given the mass fractions of proeutectoid ferrite and pearlite. From Equation 9.20

$$W_p = 0.714 = \frac{C_0' - 0.022}{0.74}$$

which yields $C_0' = 0.55$ wt% C.

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9.54 *The mass fractions of total ferrite and total cementite in an iron-carbon alloy are 0.88 and 0.12, respectively. Is this a hypoeutectoid or hypereutectoid alloy? Why?*

Solution

In this problem we are given values of W_α and W_{Fe_3C} for an iron-carbon alloy (0.88 and 0.12, respectively), and then are asked to specify whether the alloy is hypoeutectoid or hypereutectoid. Employment of the lever rule for total α leads to

$$W_\alpha = 0.88 = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_\alpha} = \frac{6.70 - C_0}{6.70 - 0.022}$$

Now, solving for C_0, the alloy composition, leads to C_0 = 0.82 wt% C. Therefore, the alloy is *hypereutectoid* since C_0 is greater than 0.76 wt% C.

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9.55 *The microstructure of an iron-carbon alloy consists of proeutectoid ferrite and pearlite; the mass fractions of these microconstituents are 0.20 and 0.80, respectively. Determine the concentration of carbon in this alloy.*

Solution

We are asked in this problem to determine the concentration of carbon in an alloy for which $W_{\alpha'} = 0.20$ and $W_p = 0.80$. If we let C_0' equal the carbon concentration in the alloy, employment of the appropriate lever rule expression, Equation 9.20, leads to

$$W_p = \frac{C_0' - 0.022}{0.74} = 0.80$$

Solving for C_0' yields $C_0' = 0.61$ wt% C.

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9.56 *Consider 2.0 kg of a 99.6 wt% Fe–0.4 wt% C alloy that is cooled to a temperature just below the eutectoid.*

(a) How many kilograms of proeutectoid ferrite form?

(b) How many kilograms of eutectoid ferrite form?

(c) How many kilograms of cementite form?

Solution

In this problem we are asked to consider 2.0 kg of a 99.6 wt% Fe-0.4 wt% C alloy that is cooled to a temperature below the eutectoid.

(a) Equation 9.21 must be used in computing the amount of proeutectoid ferrite that forms. Thus,

$$W_{\alpha'} = \frac{0.76 - C_0'}{0.74} = \frac{0.76 - 0.40}{0.74} = 0.49$$

Or, (0.49)(2.0 kg) = 0.98 kg of proeutectoid ferrite forms.

(b) In order to determine the amount of eutectoid ferrite, it first becomes necessary to compute the amount of total ferrite using the lever rule applied entirely across the $\alpha + Fe_3C$ phase field, as

$$W_{\alpha} = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_{\alpha}} = \frac{6.70 - 0.40}{6.70 - 0.022} = 0.94$$

which corresponds to (0.94)(2.0 kg) = 1.88 kg. Now, the amount of eutectoid ferrite is just the difference between total and proeutectoid ferrites, or

$$1.88 \text{ kg} - 0.98 \text{ kg} = 0.90 \text{ kg}$$

(c) With regard to the amount of cementite that forms, again application of the lever rule across the entirety of the $\alpha + Fe_3C$ phase field, leads to

$$W_{Fe_3C} = \frac{C_0 - C_{\alpha}}{C_{Fe_3C} - C_{\alpha}} = \frac{0.40 - 0.022}{6.70 - 0.022} = 0.057$$

which amounts to (0.057)(2.0 kg) = 0.114 kg cementite in the alloy.

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9.57 *Compute the maximum mass fraction of proeutectoid cementite possible for a hypereutectoid iron–carbon alloy.*

Solution

This problem asks that we compute the maximum mass fraction of proeutectoid cementite possible for a hypereutectoid iron-carbon alloy. This requires that we utilize Equation 9.23 with C_1' = 2.14 wt% C, the maximum solubility of carbon in austenite. Thus,

$$W_{Fe_3C'} = \frac{C_1' - 0.76}{5.94} = \frac{2.14 - 0.76}{5.94} = 0.232$$

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9.58 *Is it possible to have an iron-carbon alloy for which the mass fractions of total ferrite and proeutectoid cementite are 0.846 and 0.049, respectively? Why or why not?*

Solution

This problem asks if it is possible to have an iron-carbon alloy for which $W_\alpha = 0.846$ and $W_{Fe_3C'} = 0.049$. In order to make this determination, it is necessary to set up lever rule expressions for these two mass fractions in terms of the alloy composition, then to solve for the alloy composition of each; if both alloy composition values are equal, then such an alloy is possible. The expression for the mass fraction of total ferrite is

$$W_\alpha = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_\alpha} = \frac{6.70 - C_0}{6.70 - 0.022} = 0.846$$

Solving for this C_0 yields $C_0 = 1.05$ wt% C. Now for $W_{Fe_3C'}$ we utilize Equation 9.23 as

$$W_{Fe_3C'} = \frac{C_1' - 0.76}{5.94} = 0.049$$

This expression leads to $C_1' = 1.05$ wt% C. And, since $C_0 = C_1'$, this alloy *is possible*.

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9.59 *Is it possible to have an iron-carbon alloy for which the mass fractions of total cementite and pearlite are 0.039 and 0.417, respectively? Why or why not?*

Solution

This problem asks if it is possible to have an iron-carbon alloy for which $W_{Fe_3C} = 0.039$ and $W_p = 0.417$. In order to make this determination, it is necessary to set up lever rule expressions for these two mass fractions in terms of the alloy composition, then to solve for the alloy composition of each; if both alloy composition values are equal, then such an alloy is possible. The expression for the mass fraction of total cementite is

$$W_{Fe_3C} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} = \frac{C_0 - 0.022}{6.70 - 0.022} = 0.039$$

Solving for this C_0 yields $C_0 = 0.28$ wt% C. Therefore, this alloy is hypoeutectoid since C_0 is less than the eutectoid composition (0.76 wt%). Thus, it is necessary to use Equation 9.20 for W_p as

$$W_p = \frac{C'_0 - 0.022}{0.74} = 0.417$$

This expression leads to $C'_0 = 0.33$ wt% C. Since C_0 and C'_0 are different, this alloy is *not possible*.

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9.60 *Compute the mass fraction of eutectoid ferrite in an iron-carbon alloy that contains 0.43 wt% C.*

Solution

In order to solve this problem it is necessary to compute mass fractions of total and proeutectoid ferrites, and then to subtract the latter from the former. To calculate the mass fraction of total ferrite, it is necessary to use the lever rule and a tie line that extends across the entire $\alpha + Fe_3C$ phase field as

$$W_{\alpha} = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_{\alpha}} = \frac{6.70 - 0.43}{6.70 - 0.022} = 0.939$$

Now, for the mass fraction of proeutectoid ferrite we use Equation 9.21 as

$$W_{\alpha'} = \frac{0.76 - C_0' -}{0.74} = \frac{0.76 - 0.43}{0.74} = 0.446$$

And, finally, the mass fraction of eutectoid ferrite $W_{\alpha''}$ is just

$$W_{\alpha''} = W_{\alpha} - W_{\alpha'} = 0.939 - 0.446 = 0.493$$

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9.61 *The mass fraction of* eutectoid *cementite in an iron-carbon alloy is 0.104. On the basis of this information, is it possible to determine the composition of the alloy? If so, what is its composition? If this is not possible, explain why.*

Solution

This problem asks whether or not it is possible to determine the composition of an iron-carbon alloy for which the mass fraction of eutectoid cementite is 0.104; and if so, to calculate the composition. Yes, it is possible to determine the alloy composition; and, in fact, there are two possible answers. For the first, the eutectoid cementite exists in addition to proeutectoid cementite. For this case the mass fraction of eutectoid cementite ($W_{Fe_3C''}$) is just the difference between total cementite and proeutectoid cementite mass fractions; that is

$$W_{Fe_3C''} = W_{Fe_3C} - W_{Fe_3C'}$$

Now, it is possible to write expressions for W_{Fe_3C} (of the form of Equation 9.12) and $W_{Fe_3C'}$ (Equation 9.23) in terms of C_0, the alloy composition. Thus,

$$W_{Fe_3C''} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} - \frac{C_0 - 0.76}{5.94}$$

$$= \frac{C_0 - 0.022}{6.70 - 0.022} - \frac{C_0 - 0.76}{5.94} = 0.104$$

And, solving for C_0 yields $C_0 = 1.11$ wt% C.

For the second possibility, we have a hypoeutectoid alloy wherein all of the cementite is eutectoid cementite. Thus, it is necessary to set up a lever rule expression wherein the mass fraction of total cementite is 0.104. Therefore,

$$W_{Fe_3C} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} = \frac{C_0 - 0.022}{6.70 - 0.022} = 0.104$$

And, solving for C_0 yields $C_0 = 0.72$ wt% C.

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9.62 *The mass fraction of* eutectoid *ferrite in an iron-carbon alloy is 0.82. On the basis of this information, is it possible to determine the composition of the alloy? If so, what is its composition? If this is not possible, explain why.*

Solution

This problem asks whether or not it is possible to determine the composition of an iron-carbon alloy for which the mass fraction of eutectoid ferrite is 0.82; and if so, to calculate the composition. Yes, it is possible to determine the alloy composition; and, in fact, there are two possible answers. For the first, the eutectoid ferrite exists in addition to proeutectoid ferrite. For this case the mass fraction of eutectoid ferrite ($W_{\alpha''}$) is just the difference between total ferrite and proeutectoid ferrite mass fractions; that is

$$W_{\alpha''} = W_{\alpha} - W_{\alpha'}$$

Now, it is possible to write expressions for W_{α} (of the form of Equation 9.12) and $W_{\alpha'}$ (Equation 9.21) in terms of C_0, the alloy composition. Thus,

$$W_{\alpha''} = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_{\alpha}} - \frac{0.76 - C_0}{0.74}$$

$$= \frac{6.70 - C_0}{6.70 - 0.022} - \frac{0.76 - C_0}{0.74} = 0.82$$

And, solving for C_0 yields $C_0 = 0.70$ wt% C.

For the second possibility, we have a hypereutectoid alloy wherein all of the ferrite is eutectoid ferrite. Thus, it is necessary to set up a lever rule expression wherein the mass fraction of total ferrite is 0.82. Therefore,

$$W_{\alpha} = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_{\alpha}} = \frac{6.70 - C_0}{6.70 - 0.022} = 0.82$$

And, solving for C_0 yields $C_0 = 1.22$ wt% C.

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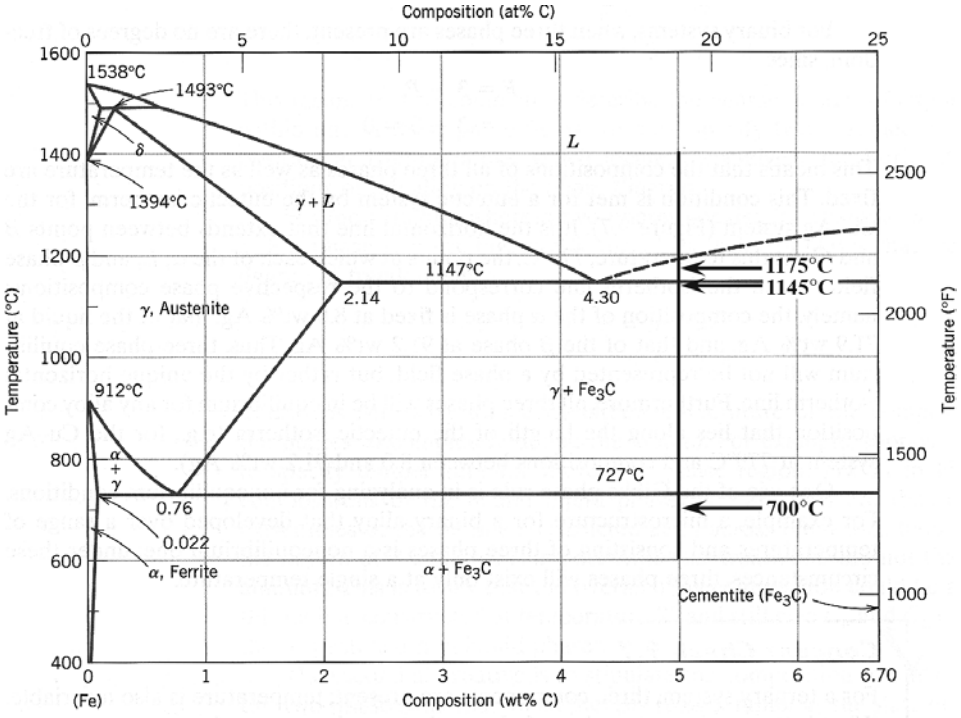
9.63 *For an iron-carbon alloy of composition 5 wt% C-95 wt% Fe, make schematic sketches of the microstructure that would be observed for conditions of very slow cooling at the following temperatures: 1175°C (2150°F), 1145°C (2095°F), and 700°C (1290°F). Label the phases and indicate their compositions (approximate).*

Solution

Below is shown the Fe-Fe_3C phase diagram (Figure 9.24). A vertical line at a composition of 5 wt% C-95 wt% Fe has been drawn, and, in addition, horizontal arrows at the three temperatures called for in the problem statement (i.e., 1175°C, 1145°C, and 700°C).



On the basis of the locations of the three temperature-composition points, schematic sketches of the respective microstructures along with phase compositions are represented as follows:

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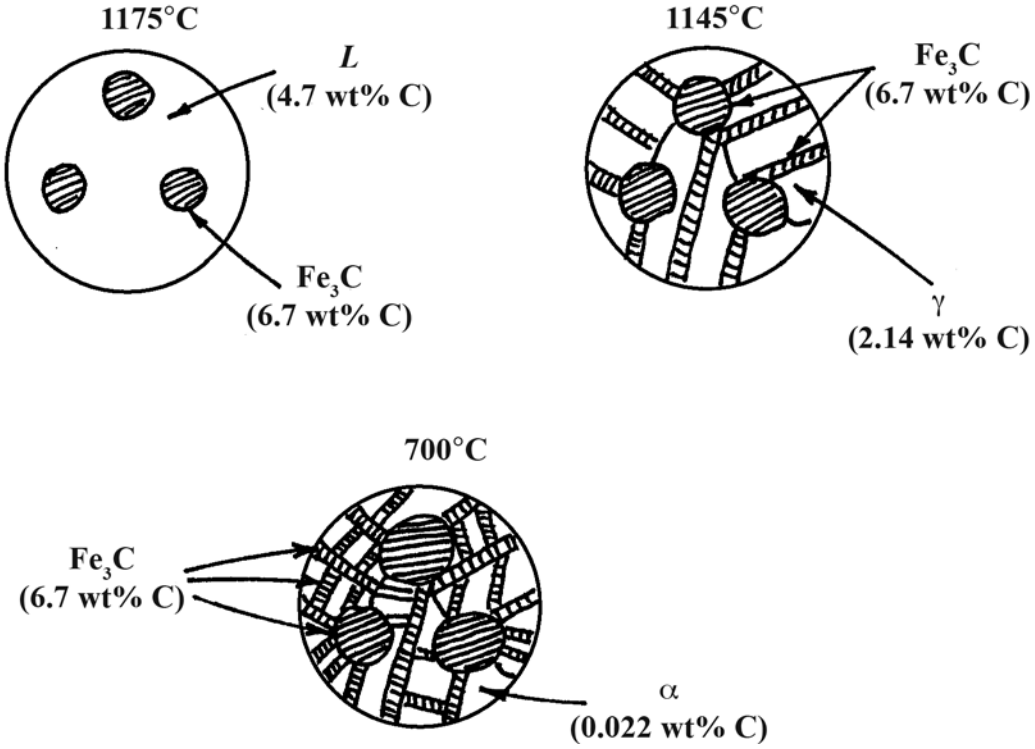

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9.64 *Often, the properties of multiphase alloys may be approximated by the relationship*

$$E\,(\text{alloy}) = E_\alpha V_\alpha + E_\beta V_\beta \qquad (9.24)$$

where E represents a specific property (modulus of elasticity, hardness, etc.), and V is the volume fraction. The subscripts α and β denote the existing phases or microconstituents. Employ the relationship above to determine the approximate Brinell hardness of a 99.80 wt% Fe–0.20 wt% C alloy. Assume Brinell hardnesses of 80 and 280 for ferrite and pearlite, respectively, and that volume fractions may be approximated by mass fractions.

Solution

This problem asks that we determine the approximate Brinell hardness of a 99.80 wt% Fe-0.20 wt% C alloy, using a relationship similar to Equation 9.24. First, we compute the mass fractions of pearlite and proeutectoid ferrite using Equations 9.20 and 9.21, as

$$W_p = \frac{C_0' - 0.022}{0.74} = \frac{0.20 - 0.022}{0.74} = 0.24$$

$$W_{\alpha'} = \frac{0.76 - C_0'}{0.74} = \frac{0.76 - 0.20}{0.74} = 0.76$$

Now, we compute the Brinell hardness of the alloy using a modified form of Equation 9.24 as

$$\text{HB}_{\text{alloy}} = \text{HB}_{\alpha'} W_{\alpha'} + \text{HB}_p W_p$$

$$= (80)(0.76) + (280)(0.24) = 128$$

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The Influence of Other Alloying Elements

9.65 *A steel alloy contains 97.5 wt% Fe, 2.0 wt% Mo, and 0.5 wt% C.*

(a) What is the eutectoid temperature of this alloy?

(b) What is the eutectoid composition?

(c) What is the proeutectoid phase?

Assume that there are no changes in the positions of other phase boundaries with the addition of Mo.

Solution

(a) From Figure 9.34, the eutectoid temperature for 2.0 wt% Mo is approximately 850°C.

(b) From Figure 9.35, the eutectoid composition is approximately 0.22 wt% C.

(c) Since the carbon concentration of the alloy (0.5 wt%) is greater than the eutectoid (0.22 wt% C), cementite is the proeutectoid phase.

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9.66 *A steel alloy is known to contain 93.8 wt% Fe, 6.0 wt% Ni, and 0.2 wt% C.*

(a) What is the approximate eutectoid temperature of this alloy?

(b) What is the proeutectoid phase when this alloy is cooled to a temperature just below the eutectoid?

(c) Compute the relative amounts of the proeutectoid phase and pearlite.

Assume that there are no alterations in the positions of other phase boundaries with the addition of Ni.

Solution

(a) From Figure 9.34, the eutectoid temperature for 6.0 wt% Ni is approximately 650°C (1200°F).

(b) From Figure 9.35, the eutectoid composition is approximately 0.62 wt% C. Since the carbon concentration in the alloy (0.2 wt%) is less than the eutectoid (0.62 wt% C), the proeutectoid phase is ferrite.

(c) Assume that the α–(α + Fe_3C) phase boundary is at a negligible carbon concentration. Modifying Equation 9.21 leads to

$$W_{\alpha'} = \frac{0.62 - C_0'}{0.62 - 0} = \frac{0.62 - 0.20}{0.62} = 0.68$$

Likewise, using a modified Equation 9.20

$$W_p = \frac{C_0' - 0}{0.62 - 0} = \frac{0.20}{0.62} = 0.32$$

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CHAPTER 10

PHASE TRANSFORMATIONS IN METALS

PROBLEM SOLUTIONS

The Kinetics of Phase Transformations

10.1 *Name the two stages involved in the formation of particles of a new phase. Briefly describe each.*

Solution

The two stages involved in the formation of particles of a new phase are *nucleation* and *growth*. The nucleation process involves the formation of normally very small particles of the new phase(s) which are stable and capable of continued growth. The growth stage is simply the increase in size of the new phase particles.

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10.2 *(a) Rewrite the expression for the total free energy change for nucleation (Equation 10.1) for the case of a cubic nucleus of edge length a (instead of a sphere of radius r). Now differentiate this expression with respect to a (per Equation 10.2) and solve for both the critical cube edge length, a*, and also ΔG*.*

(b) Is ΔG greater for a cube or a sphere? Why?*

Solution

(a) This problem first asks that we rewrite the expression for the total free energy change for nucleation (analogous to Equation 10.1) for the case of a cubic nucleus of edge length a. The volume of such a cubic radius is a^3, whereas the total surface area is $6a^2$ (since there are six faces each of which has an area of a^2). Thus, the expression for ΔG is as follows:

$$\Delta G = a^3 \Delta G_v + 6a^2 \gamma$$

Differentiation of this expression with respect to a is as

$$\frac{d\Delta G}{da} = \frac{d\left(a^3 \Delta G_v\right)}{da} + \frac{d\left(6a^2 \gamma\right)}{da}$$

$$= 3a^2 \Delta G_v + 12a\gamma$$

If we set this expression equal to zero as

$$3a^2 \Delta G_v + 12a\gamma = 0$$

and then solve for a (= a*), we have

$$a^* = -\frac{4\gamma}{\Delta G_v}$$

Substitution of this expression for a in the above expression for ΔG yields an equation for ΔG* as

$$\Delta G^* = (a^*)^3 \Delta G_v + 6(a^*)^2 \gamma$$

$$= \left(-\frac{4\gamma}{\Delta G_v}\right)^3 \Delta G_v + 6\gamma \left(-\frac{4\gamma}{\Delta G_v}\right)^2$$

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$$= \frac{32\gamma^3}{(\Delta G_v)^2}$$

(b) ΔG_v for a cube—i.e., $(32)\left[\frac{\gamma^3}{(\Delta G_v)^2}\right]$—is greater that for a sphere—i.e., $\left(\frac{16\pi}{3}\right)\left[\frac{\gamma^3}{(\Delta G_v)^2}\right] = (16.8)\left[\frac{\gamma^3}{(\Delta G_v)^2}\right]$. The reason for this is that surface-to-volume ratio of a cube is greater than for a sphere.

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10.3 *If copper (which has a melting point of 1085°C) homogeneously nucleates at 849°C, calculate the critical radius given values of* -1.77×10^9 *J/m*^{3} *and 0.200 J/m*^{2}*, respectively, for the latent heat of fusion and the surface free energy.*

Solution

This problem states that copper homogeneously nucleates at 849°C, and that we are to calculate the critical radius given the latent heat of fusion (-1.77×10^9 J/m^3) and the surface free energy (0.200 J/m^2). Solution to this problem requires the utilization of Equation 10.6 as

$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{T_m - T}\right)$$

$$= \left[-\frac{(2)(0.200\ \text{J/m}^2)(1085 + 273\ \text{K})}{-1.77 \times 10^9\ \text{J/m}^3}\right]\left(\frac{1}{1085°\text{C} - 849°\text{C}}\right)$$

$$= 1.30 \times 10^{-9}\ \text{m} = 1.30\ \text{nm}$$

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10.4 *(a) For the solidification of iron, calculate the critical radius r* and the activation free energy ΔG* if nucleation is homogeneous. Values for the latent heat of fusion and surface free energy are –1.85 × 10^9 J/m^3 and 0.204 J/m^2, respectively. Use the supercooling value found in Table 10.1.*

(b) Now calculate the number of atoms found in a nucleus of critical size. Assume a lattice parameter of 0.292 nm for solid iron at its melting temperature.

Solution

(a) This portion of the problem asks that we compute r^* and ΔG^* for the homogeneous nucleation of the solidification of Fe. First of all, Equation 10.6 is used to compute the critical radius. The melting temperature for iron, found inside the front cover is 1538°C; also values of ΔH_f (-1.85×10^9 J/m^3) and γ (0.204 J/m^2) are given in the problem statement, and the supercooling value found in Table 10.1 is 295°C (or 295 K). Thus, from Equation 10.6 we have

$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{T_m - T}\right)$$

$$= \left[-\frac{(2)\left(0.204\ \text{J/m}^2\right)(1538 + 273\ \text{K})}{-1.85 \times 10^9\ \text{J/m}^3}\right]\left(\frac{1}{295\ \text{K}}\right)$$

$$= 1.35 \times 10^{-9}\,\text{m} = 1.35\ \text{nm}$$

For computation of the activation free energy, Equation 10.7 is employed. Thus

$$\Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\frac{1}{(T_m - T)^2}$$

$$= \left[\frac{(16)(\pi)\left(0.204\ \text{J/m}^2\right)^3 (1538 + 273\ \text{K})^2}{(3)\left(-1.85 \times 10^9\ \text{J/m}^3\right)^2}\right]\left[\frac{1}{(295\ \text{K})^2}\right]$$

$$= 1.57 \times 10^{-18}\ \text{J}$$

(b) In order to compute the number of atoms in a nucleus of critical size (assuming a spherical nucleus of radius r^*), it is first necessary to determine the number of unit cells, which we then multiply by the number of atoms per unit cell. The number of unit cells found in this critical nucleus is just the ratio of critical nucleus and unit cell volumes. Inasmuch as iron has the BCC crystal structure, its unit cell volume is just a^3 where a is the unit cell

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length (i.e., the lattice parameter); this value is 0.292 nm, as cited in the problem statement. Therefore, the number of unit cells found in a radius of critical size is just

$$\#\ \text{unit cells/particle} = \frac{\frac{4}{3}\pi r^{*3}}{a^3}$$

$$= \frac{\left(\frac{4}{3}\right)(\pi)(1.35\ \text{nm})^3}{(0.292\ \text{nm})^3} = 414\ \text{unit cells}$$

Inasmuch as 2 atoms are associated with each BCC unit cell, the total number of atoms per critical nucleus is just

$$(414\ \text{unit cells/critical nucleus})(2\ \text{atoms/unit cell}) = 828\ \text{atoms/critical nucleus}$$

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10.5 *(a) Assume for the solidification of iron (Problem 10.4) that nucleation is homogeneous, and the number of stable nuclei is 10^6 nuclei per cubic meter. Calculate the critical radius and the number of stable nuclei that exist at the following degrees of supercooling: 200 K and 300 K.*

(b) What is significant about the magnitudes of these critical radii and the numbers of stable nuclei?

Solution

(a) For this part of the problem we are asked to calculate the critical radius for the solidification of iron (per Problem 10.4), for 200 K and 300 K degrees of supercooling, and assuming that the there are 10^6 nuclei per meter cubed for homogeneous nucleation. In order to calculate the critical radii, we replace the $T_m - T$ term in Equation 10.6 by the degree of supercooling (denoted as ΔT) cited in the problem.

For 200 K supercooling,

$$r^*_{200} = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{\Delta T}\right)$$

$$= \left[-\frac{(2)\left(0.204\ \text{J/m}^2\right)(1538 + 273\ \text{K})}{-1.85 \times 10^9\ \text{J/m}^3}\right]\left(\frac{1}{200\ \text{K}}\right)$$

$$= 2.00 \times 10^{-9}\ \text{m} = 2.00\ \text{nm}$$

And, for 300 K supercooling,

$$r^*_{300} = \left[-\frac{(2)\left(0.204\ \text{J/m}^2\right)(1538 + 273\ \text{K})}{-1.85 \times 10^9\ \text{J/m}^3}\right]\left(\frac{1}{300\ \text{K}}\right)$$

$$= 1.33 \times 10^{-9}\ \text{m} = 1.33\ \text{nm}$$

In order to compute the number of stable nuclei that exist at 200 K and 300 K degrees of supercooling, it is necessary to use Equation 10.8. However, we must first determine the value of K_1 in Equation 10.8, which in turn requires that we calculate ΔG^* at the homogeneous nucleation temperature using Equation 10.7; this was done in Problem 10.4, and yielded a value of $\Delta G^* = 1.57 \times 10^{-18}$ J. Now for the computation of K_1, using the value of n^* for at the homogenous nucleation temperature (10^6 nuclei/m^3):

$$K_1 = \frac{n^*}{\exp\left(-\frac{\Delta G^*}{kT}\right)}$$

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$$= \frac{10^6 \text{ nuclei/m}^3}{\exp\left[-\dfrac{1.57 \times 10^{-18} \text{ J}}{(1.38 \times 10^{-23} \text{ J/atom-K})(1538°\text{C} - 295°\text{C})}\right]}$$

$$= 5.62 \times 10^{45} \text{ nuclei/m}^3$$

Now for 200 K supercooling, it is first necessary to recalculate the value ΔG^* of using Equation 10.7, where, again, the $T_m - T$ term is replaced by the number of degrees of supercooling, denoted as ΔT, which in this case is 200 K. Thus

$$\Delta G^*_{200} = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\frac{1}{(\Delta T)^2}$$

$$= \left[\frac{(16)(\pi)(0.204 \text{ J/m}^2)^3 (1538 + 273 \text{ K})^2}{(3)(-1.85 \times 10^9 \text{ J/m}^3)^2}\right]\left[\frac{1}{(200 \text{ K})^2}\right]$$

$$= 3.41 \times 10^{-18} \text{ J}$$

And, from Equation 10.8, the value of n^* is

$$n^*_{200} = K_1 \exp\left(-\frac{\Delta G^*_{200}}{kT}\right)$$

$$= (5.62 \times 10^{45} \text{ nuclei/m}^3)\exp\left[-\frac{3.41 \times 10^{-18} \text{ J}}{(1.38 \times 10^{-23} \text{ J/atom-K})(1538 \text{ K} - 200 \text{ K})}\right]$$

$$= 3.5 \times 10^{-35} \text{ stable nuclei}$$

Now, for 300 K supercooling the value of ΔG^* is equal to

$$\Delta G^*_{300} = \left[\frac{(16)(\pi)(0.204 \text{ J/m}^2)^3 (1538 + 273 \text{ K})^2}{(3)(-1.85 \times 10^9 \text{ J/m}^3)^2}\right]\left[\frac{1}{(300 \text{ K})^2}\right]$$

$$= 1.51 \times 10^{-18} \text{ J}$$

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from which we compute the number of stable nuclei at 300 K of supercooling as

$$n_{300}^{*} = K_1 \exp\left(-\frac{\Delta G_{300}^{*}}{kT}\right)$$

$$n^{*} = \left(5.62 \times 10^{45}\ \text{nuclei/m}^3\right)\exp\left[-\frac{1.51 \times 10^{-18}\ \text{J}}{\left(1.38 \times 10^{-23}\ \text{J/atom-K}\right)(1538\ \text{K} - 300\ \text{K})}\right]$$

$$= 2.32 \times 10^{7}\ \text{stable nuclei}$$

(b) Relative to critical radius, r^* for 300 K supercooling is slightly smaller that for 200 K (1.33 nm versus 2.00 nm). [From Problem 10.4, the value of r^* at the homogeneous nucleation temperature (295 K) was 1.35 nm.] More significant, however, are the values of n^* at these two degrees of supercooling, which are dramatically different—3.5×10^{-35} stable nuclei at $\Delta T = 200$ K, versus 2.32×10^{7} stable nuclei at $\Delta T = 300$ K!

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10.6 *For some transformation having kinetics that obey the Avrami equation (Equation 10.17), the parameter n is known to have a value of 1.7. If, after 100 s, the reaction is 50% complete, how long (total time) will it take the transformation to go to 99% completion?*

Solution

This problem calls for us to compute the length of time required for a reaction to go to 99% completion. It first becomes necessary to solve for the parameter k in Equation 10.17. In order to do this it is best manipulate the equation such that k is the dependent variable. We first rearrange Equation 10.17 as

$$\exp\left(-kt^n\right) = 1 - y$$

and then take natural logarithms of both sides:

$$-kt^n = \ln(1 - y)$$

Now solving for k gives

$$k = -\frac{\ln (1 - y)}{t^n}$$

And, from the problem statement, for $y = 0.50$ when $t = 100$ s and given that $n = 1.7$, the value of k is equal to

$$k = -\frac{\ln (1 - 0.5)}{(100\ \text{s})^{1.7}} = 2.76 \times 10^{-4}$$

We now want to manipulate Equation 10.17 such that t is the dependent variable. The above equation may be written in the form:

$$t^n = -\frac{\ln (1 - y)}{k}$$

And solving this expression for t leads to

$$t = \left[-\frac{\ln (1 - y)}{k}\right]^{1/n}$$

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Now, using this equation and the value of k determined above, the time to 99% transformation completion is equal to

$$t = \left[-\frac{\ln (1 - 0.99)}{2.76 \times 10^{-4}} \right]^{1/1.7} = 305 \text{ s}$$

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10.7 *Compute the rate of some reaction that obeys Avrami kinetics, assuming that the constants n and k have values of 3.0 and 7×10^{-3}, respectively, for time expressed in seconds.*

Solution

This problem asks that we compute the rate of some reaction given the values of n and k in Equation 10.17. Since the reaction rate is defined by Equation 10.18, it is first necessary to determine $t_{0.5}$, or the time necessary for the reaction to reach $y = 0.5$. We must first manipulate Equation 10.17 such that t is the dependent variable. We first rearrange Equation 10.17 as

$$\exp\left(-kt^n\right) = 1 - y$$

and then take natural logarithms of both sides:

$$-kt^n = \ln(1 - y)$$

which my be rearranged so as to read

$$t^n = -\frac{\ln (1 - y)}{k}$$

Now, solving for t from this expression leads to

$$t = \left[-\frac{\ln (1 - y)}{k}\right]^{1/n}$$

For $t_{0.5}$ this equation takes the form

$$t_{0.5} = \left[-\frac{\ln (1 - 0.5)}{k}\right]^{1/n}$$

And, incorporation of values for n and k given in the problem statement (3.0 and 7×10^{-3}, respectively), then

$$t_{0.5} = \left[-\frac{\ln (1 - 0.5)}{7 \times 10^{-3}}\right]^{1/3.0} = 4.63 \text{ s}$$

Now, the rate is computed using Equation 10.18 as

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$$\text{rate} = \frac{1}{t_{0.5}} = \frac{1}{4.63\ \text{s}} = 0.216\ \ \text{s}^{-1}$$

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10.8 *It is known that the kinetics of recrystallization for some alloy obey the Avrami equation and that the value of n in the exponential is 2.5. If, at some temperature, the fraction recrystallized is 0.40 after 200 min, determine the rate of recrystallization at this temperature.*

Solution

This problem gives us the value of y (0.40) at some time t (200 min), and also the value of n (2.5) for the recrystallization of an alloy at some temperature, and then asks that we determine the rate of recrystallization at this same temperature. It is first necessary to calculate the value of k. We first rearrange Equation 10.17 as

$$\exp\left(-kt^n\right) = 1 - y$$

and then take natural logarithms of both sides:

$$-kt^n = \ln(1 - y)$$

Now solving for k gives

$$k = -\frac{\ln (1 - y)}{t^n}$$

which, using the values cited above for y, n, and t yields

$$k = -\frac{\ln (1 - 0.40)}{(200 \text{ min})^{2.5}} = 9.0 \times 10^{-7}$$

At this point we want to compute $t_{0.5}$, the value of t for $y = 0.5$, which means that it is necessary to establish a form of Equation 10.17 in which t is the dependent variable. From one of the above equations

$$t^n = -\frac{\ln (1 - y)}{k}$$

And solving this expression for t leads to

$$t = \left[-\frac{\ln (1 - y)}{k}\right]^{1/n}$$

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For $t_{0.5}$, this equation takes the form

$$t_{0.5} = \left[-\frac{\ln (1 - 0.5)}{k} \right]^{1/n}$$

and incorporation of the value of k determined above, as well as the value of n cited in the problem statement (2.5), then $t_{0.5}$ is equal to

$$t_{0.5} = \left[-\frac{\ln (1 - 0.5)}{9.0 \times 10^{-7}} \right]^{1/2.5} = 226.3 \text{ min}$$

Therefore, from Equation 10.18, the rate is just

$$\text{rate} = \frac{1}{t_{0.5}} = \frac{1}{226.3 \text{ min}} = 4.42 \times 10^{-3} \text{ (min)}^{-1}$$

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10.9 *The kinetics of the austenite-to-pearlite transformation obey the Avrami relationship. Using the fraction transformed–time data given here, determine the total time required for 95% of the austenite to transform to pearlite:*

Fraction Transformed	***Time* (*s*)**
0.2	*12.6*
0.8	*28.2*

Solution

The first thing necessary is to set up two expressions of the form of Equation 10.17, and then to solve simultaneously for the values of n and k. In order to expedite this process, we will rearrange and do some algebraic manipulation of Equation 10.17. First of all, we rearrange as follows:

$$1 - y = \exp\left(-kt^n\right)$$

Now taking natural logarithms

$$\ln\,(1 - y) = -kt^n$$

Or

$$-\ln\,(1 - y) = kt^n$$

which may also be expressed as

$$\ln\left(\frac{1}{1 - y}\right) = kt^n$$

Now taking natural logarithms again, leads to

$$\ln\left[\ln\left(\frac{1}{1 - y}\right)\right] = \ln\,k + n\,\ln t$$

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which is the form of the equation that we will now use. Using values cited in the problem statement, the two equations are thus

$$\ln\left\{\ln\left[\frac{1}{1-0.2}\right]\right\} = \ln k + n\ln(12.6\text{ s})$$

$$\ln\left\{\ln\left[\frac{1}{1-0.8}\right]\right\} = \ln k + n\ln(28.2\text{ s})$$

Solving these two expressions simultaneously for n and k yields $n = 2.453$ and $k = 4.46 \times 10^{-4}$.

Now it becomes necessary to solve for the value of t at which $y = 0.95$. One of the above equations—viz

$$-\ln(1-y) = kt^n$$

may be rewritten as

$$t^n = -\frac{\ln(1-y)}{k}$$

And solving for t leads to

$$t = \left[-\frac{\ln(1-y)}{k}\right]^{1/n}$$

Now incorporating into this expression values for n and k determined above, the time required for 95% austenite transformation is equal to

$$t = \left[-\frac{\ln(1-0.95)}{4.64 \times 10^{-4}}\right]^{1/2.453} = 35.7\text{ s}$$

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10.10 *The fraction recrystallized–time data for the recrystallization at 600°C of a previously deformed steel are tabulated here. Assuming that the kinetics of this process obey the Avrami relationship, determine the fraction recrystallized after a total time of 22.8 min.*

Fraction Recrystallized	***Time (min)***
0.20	*13.1*
0.70	*29.1*

Solution

The first thing necessary is to set up two expressions of the form of Equation 10.17, and then to solve simultaneously for the values of n and k. In order to expedite this process, we will rearrange and do some algebraic manipulation of Equation 10.17. First of all, we rearrange as follows:

$$1 - y = \exp\left(-kt^n\right)$$

Now taking natural logarithms

$$\ln (1 - y) = -kt^n$$

Or

$$-\ln (1 - y) = kt^n$$

which may also be expressed as

$$\ln\left(\frac{1}{1 - y}\right) = kt^n$$

Now taking natural logarithms again, leads to

$$\ln\left[\ln\left(\frac{1}{1 - y}\right)\right] = \ln k + n \ln t$$

which is the form of the equation that we will now use. The two equations are thus

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$$\ln\left\{\ln\left[\frac{1}{1-0.20}\right]\right\} = \ln k + n\ln(13.1\ \text{min})$$

$$\ln\left\{\ln\left[\frac{1}{1-0.70}\right]\right\} = \ln k + n\ln(29.1\ \text{min})$$

Solving these two expressions simultaneously for n and k yields $n = 2.112$ and $k = 9.75 \times 10^{-4}$.

Now it becomes necessary to solve for y when $t = 22.8$ min. Application of Equation 10.17 leads to

$$y = 1 - \exp\left(-kt^n\right)$$

$$= 1 - \exp\left[-\left(9.75 \times 10^{-4}\right)(22.8\ \text{min})^{2.112}\right] = 0.51$$

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10.11 *(a) From the curves shown in Figure 10.11 and using Equation 10.18, determine the rate of recrystallization for pure copper at the several temperatures.*

(b) Make a plot of ln(rate) versus the reciprocal of temperature (in K^{-1}), and determine the activation energy for this recrystallization process. (See Section 5.5.)

(c) By extrapolation, estimate the length of time required for 50% recrystallization at room temperature, 20°C (293 K).

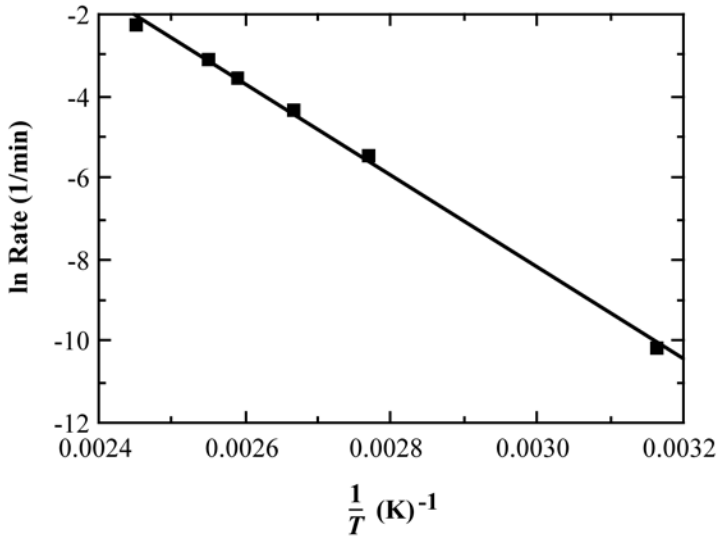
Solution

This problem asks us to consider the percent recrystallized versus logarithm of time curves for copper shown in Figure 10.11.

(a) The rates at the different temperatures are determined using Equation 10.18, which rates are tabulated below:

Temperature (°C)	Rate $(min)^{-1}$
135	0.105
119	4.4×10^{-2}
113	2.9×10^{-2}
102	1.25×10^{-2}
88	4.2×10^{-3}
43	3.8×10^{-5}

(b) These data are plotted below.



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The activation energy, Q, is related to the slope of the line drawn through the data points as

$$Q = -\,\text{Slope}\ (R)$$

where R is the gas constant. The slope of this line is equal to

$$\text{Slope} = \frac{\Delta \ln \text{rate}}{\Delta\left(\frac{1}{T}\right)} = \frac{\ln \text{ rate}_1 - \ln \text{ rate}_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

Let us take $1/T_1 = 0.0025\ \text{K}^{-1}$ and $1/T_2 = 0.0031\ \text{K}^{-1}$; the corresponding ln rate values are ln rate_1 = -2.6 and ln rate_2 = -9.4. Thus, using these values, the slope is equal to

$$\text{Slope} = \frac{-2.6 - (-9.4)}{0.0025\ \text{K}^{-1} - 0.0031\ \text{K}^{-1}} = -1.133 \times 10^4\ \text{K}$$

And, finally the activation energy is

$$Q = -\ (\text{Slope})(R) = -\left(-1.133 \times 10^4\ \text{K}^{-1}\right)(8.31\ \text{J/mol - K})$$

$$= 94{,}150\ \text{J/mol}$$

(c) At room temperature (20°C), $1/T = 1/(20 + 273\ \text{K}) = 3.41 \times 10^{-3}\ \text{K}^{-1}$. Extrapolation of the data in the plot to this $1/T$ value gives

$$\ln (\text{rate}) \cong -12.8$$

which leads to

$$\text{rate} \cong \exp(-12.8) = 2.76 \times 10^{-6}\ (\text{min})^{-1}$$

But since

$$\text{rate} = \frac{1}{t_{0.5}}$$

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$$t_{0.5} = \frac{1}{\text{rate}} = \frac{1}{2.76 \times 10^{-6}\ (\text{min})^{-1}}$$

$$= 3.62 \times 10^{5}\ \text{min} = 250\ \text{days}$$

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10.12 *Determine values for the constants n and k (Equation 10.17) for the recrystallization of copper (Figure 10.11) at 102°C.*

Solution

In this problem we are asked to determine, from Figure 10.11, the values of the constants n and k (Equation 10.17) for the recrystallization of copper at 102°C. One way to solve this problem is to take two values of percent recrystallization (which is just 100y, Equation 10.17) and their corresponding time values, then set up two simultaneous equations, from which n and k may be determined. In order to expedite this process, we will rearrange and do some algebraic manipulation of Equation 10.17. First of all, we rearrange as follows:

$$1 - y = \exp\left(-kt^n\right)$$

Now taking natural logarithms

$$\ln (1 - y) = -kt^n$$

Or

$$-\ln (1 - y) = kt^n$$

which may also be expressed as

$$\ln\left(\frac{1}{1 - y}\right) = kt^n$$

Now taking natural logarithms again, leads to

$$\ln\left[\ln\left(\frac{1}{1 - y}\right)\right] = \ln k + n \ln t$$

which is the form of the equation that we will now use. From the 102°C curve of Figure 10.11, let us arbitrarily choose two percent recrystallized values, 20% and 80% (i.e., $y_1 = 0.20$ and $y_2 = 0.80$). Their corresponding time values are $t_1 = 50$ min and $t_2 = 100$ min (realizing that the time axis is scaled logarithmically). Thus, our two simultaneous equations become

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$$\ln\left[\ln\left(\frac{1}{1-0.2}\right)\right] = \ln k + n \ln(50)$$

$$\ln\left[\ln\left(\frac{1}{1-0.8}\right)\right] = \ln k + n \ln(100)$$

from which we obtain the values $n = 2.85$ and $k = 3.21 \times 10^{-6}$.

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Metastable Versus Equilibrium States

10.13 *In terms of heat treatment and the development of microstructure, what are two major limitations of the iron–iron carbide phase diagram?*

Solution

Two limitations of the iron-iron carbide phase diagram are:

(1) The nonequilibrium martensite does not appear on the diagram; and

(2) The diagram provides no indication as to the time-temperature relationships for the formation of pearlite, bainite, and spheroidite, all of which are composed of the equilibrium ferrite and cementite phases.

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10.14 *(a) Briefly describe the phenomena of superheating and supercooling.*

(b) Why do these phenomena occur?

Solution

(a) Superheating and supercooling correspond, respectively, to heating or cooling above or below a phase transition temperature without the occurrence of the transformation.

(b) These phenomena occur because right at the phase transition temperature, the driving force is not sufficient to cause the transformation to occur. The driving force is enhanced during superheating or supercooling.

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Isothermal Transformation Diagrams

10.15 *Suppose that a steel of eutectoid composition is cooled to 550°C (1020°F) from 760°C (1400°F) in less than 0.5 s and held at this temperature.*

(a) How long will it take for the austenite-to-pearlite reaction to go to 50% completion? To 100% completion?

(b) Estimate the hardness of the alloy that has completely transformed to pearlite.

Solution

We are called upon to consider the isothermal transformation of an iron-carbon alloy of eutectoid composition.

(a) From Figure 10.22, a horizontal line at 550°C intersects the 50% and reaction completion curves at about 2.5 and 6 seconds, respectively; these are the times asked for in the problem statement.

(b) The pearlite formed will be fine pearlite. From Figure 10.30*a*, the hardness of an alloy of composition 0.76 wt% C that consists of fine pearlite is about 265 HB (27 HRC).

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10.16 *Briefly cite the differences between pearlite, bainite, and spheroidite relative to microstructure and mechanical properties.*

Solution

The microstructures of pearlite, bainite, and spheroidite all consist of α-ferrite and cementite phases. For pearlite, the two phases exist as layers which alternate with one another. Bainite consists of very fine and parallel needle-shaped particles of cementite that are surrounded an α-ferrite matrix. For spheroidite, the matrix is ferrite, and the cementite phase is in the shape of sphere-shaped particles.

Bainite is harder and stronger than pearlite, which, in turn, is harder and stronger than spheroidite.

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10.17 *What is the driving force for the formation of spheroidite?*

Solution

The driving force for the formation of spheroidite is the net reduction in ferrite-cementite phase boundary area.

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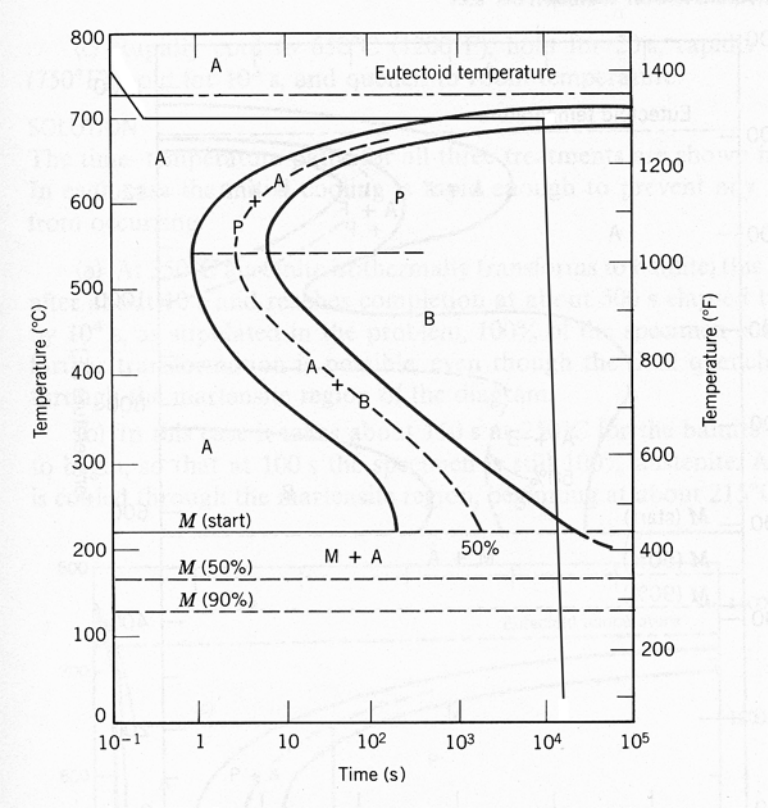
10.18 *Using the isothermal transformation diagram for an iron–carbon alloy of eutectoid composition (Figure 10.22), specify the nature of the final microstructure (in terms of microconstituents present and approximate percentages of each) of a small specimen that has been subjected to the following time–temperature treatments. In each case assume that the specimen begins at 760°C (1400°F) and that it has been held at this temperature long enough to have achieved a complete and homogeneous austenitic structure.*

(a) Cool rapidly to 700°C (1290°F), hold for 10^4 s, then quench to room temperature.

Solution

Below is Figure 10.22 upon which is superimposed the above heat treatment.



After cooling and holding at 700°C for 10^4 s, approximately 50% of the specimen has transformed to coarse pearlite. Upon cooling to room temperature, the remaining 50% transforms to martensite. Hence, the final microstructure consists of about 50% coarse pearlite and 50% martensite.

(b) Reheat the specimen in part (a) to 700°C (1290°F) for 20 h.

Solution

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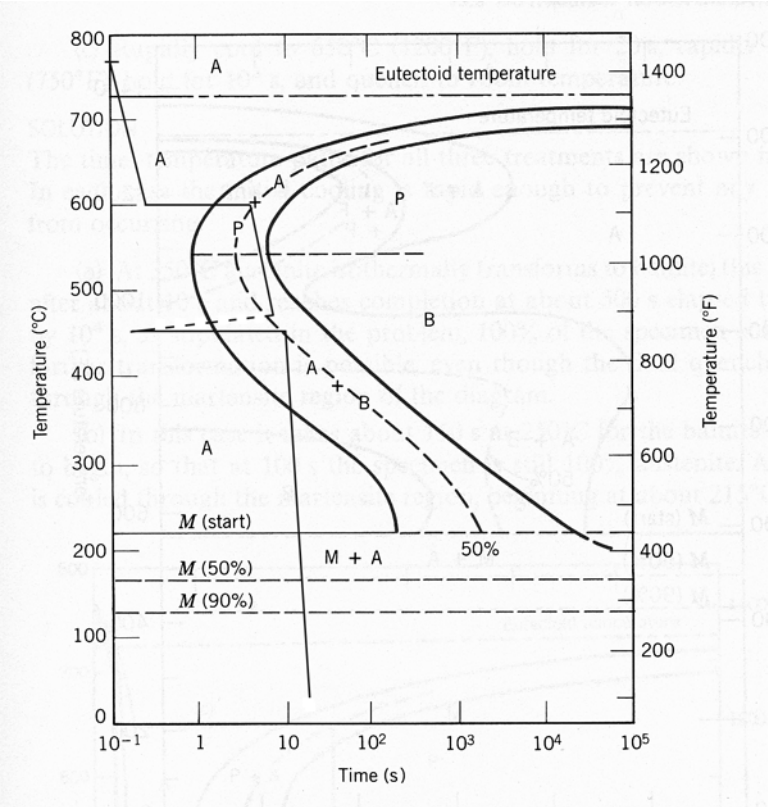
Heating to 700°C for 20 h the specimen in part (a) will transform the coarse pearlite and martensite to spheroidite.

(c) Rapidly cool to 600°C (1110°F), hold for 4 s, rapidly cool to 450°C (840°F), hold for 10 s, then quench to room temperature.

Solution

Below is Figure 10.22 upon which is superimposed the above heat treatment.



After cooling to and holding at 600°C for 4 s, approximately 50% of the specimen has transformed to pearlite (medium). During the rapid cooling to 450°C no transformations occur. At 450°C we start timing again at zero time; while holding at 450°C for 10 s, approximately 50 percent of the remaining unreacted 50% (or 25% of the original specimen) will transform to bainite. And upon cooling to room temperature, the remaining 25% of the original specimen transforms to martensite. Hence, the final microstructure consists of about 50% pearlite (medium), 25% bainite, and 25% martensite.

(d) Cool rapidly to 400°C (750°F), hold for 2 s, then quench to room temperature.

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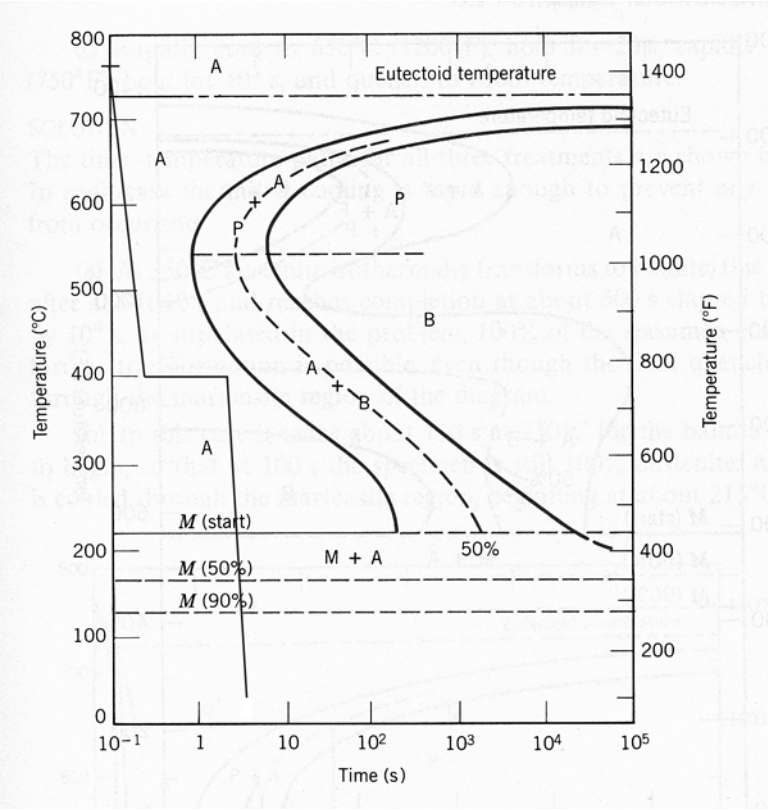
Solution

Below is Figure 10.22 upon which is superimposed the above heat treatment.



After cooling to and holding at 400°C for 2 s, no of the transformation begin lines have been crossed, and therefore, the specimen is 100% austenite. Upon cooling rapidly to room temperature, all of the specimen transforms to martensite, such that the final microstructure is 100% martensite.

(e) Cool rapidly to 400°C (750°F), hold for 20 s, then quench to room temperature.

Solution

Below is Figure 10.22 upon which is superimposed the above heat treatment.

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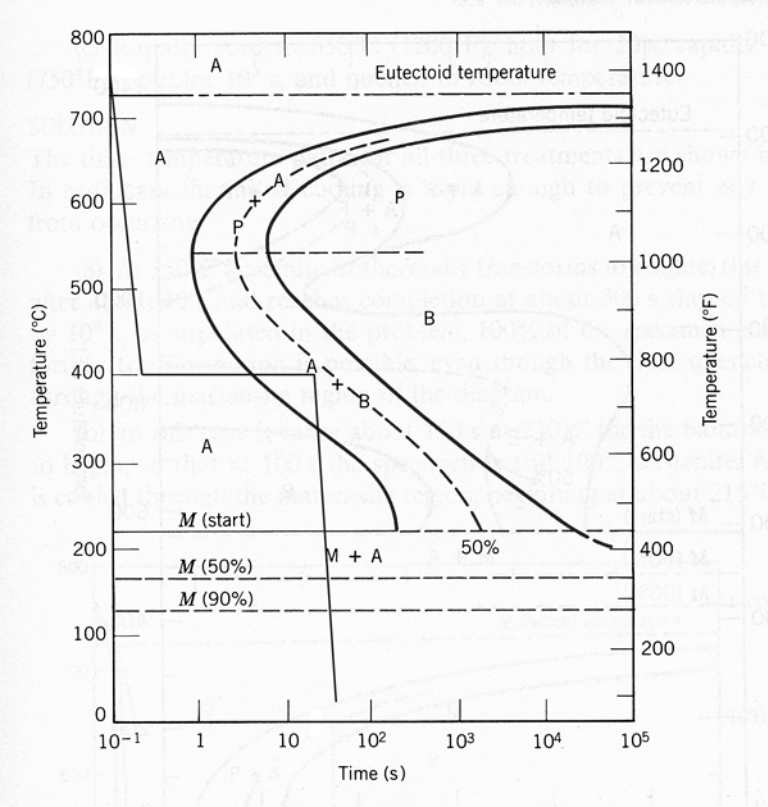

After cooling and holding at 400°C for 20 s, approximately 40% of the specimen has transformed to bainite. Upon cooling to room temperature, the remaining 60% transforms to martensite. Hence, the final microstructure consists of about 40% bainite and 60% martensite.

(f) Cool rapidly to 400°C (750°F), hold for 200 s, then quench to room temperature.

Solution

Below is Figure 10.22 upon which is superimposed the above heat treatment.

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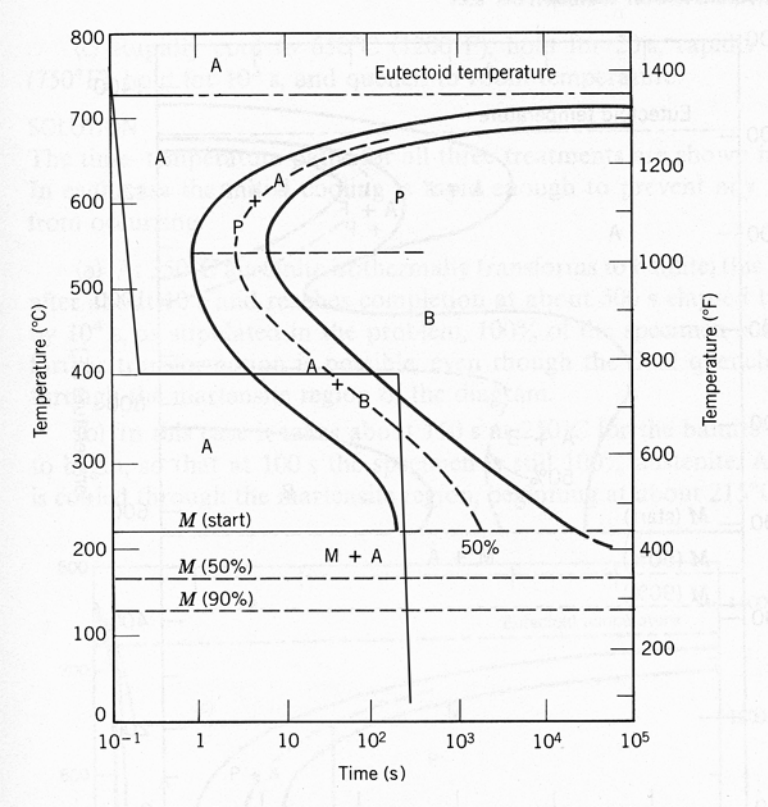

After cooling and holding at 400°C for 200 s, the entire specimen has transformed to bainite. Therefore, during the cooling to room temperature no additional transformations will occur. Hence, the final microstructure consists of 100% bainite.

(g) Rapidly cool to 575°C (1065°F), hold for 20 s, rapidly cool to 350°C (660°F), hold for 100 s, then quench to room temperature.

Solution

Below is Figure 10.22 upon which is superimposed the above heat treatment.

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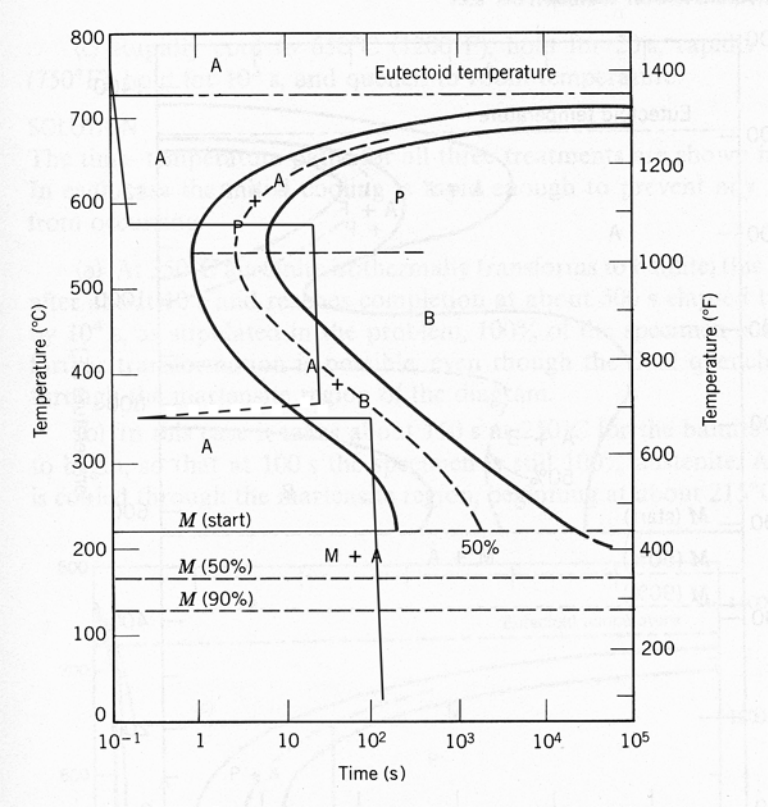

After cooling and holding at 575°C for 20 s, the entire specimen has transformed to fine pearlite. Therefore, during the second heat treatment at 350°C no additional transformations will occur. Hence, the final microstructure consists of 100% fine pearlite.

(h) Rapidly cool to 250°C (480°F), hold for 100 s, then quench to room temperature in water. Reheat to 315°C (600°F) for 1 h and slowly cool to room temperature.

Solution

Below is Figure 10.22 upon which is superimposed the above heat treatment.

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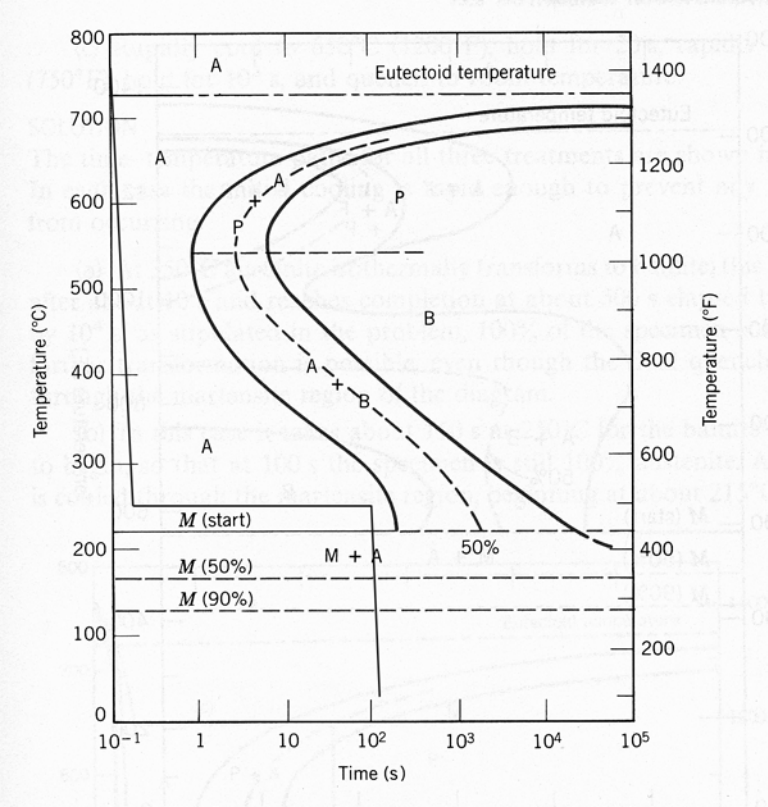

After cooling and holding at 250°C for 100 s, no transformations will have occurred—at this point, the entire specimen is still austenite. Upon rapidly cooling to room temperature in water, the specimen will completely transform to martensite. The second heat treatment (at 315°C for 1 h)—not shown on the above plot—will transform the material to tempered martensite. Hence, the final microstructure is 100% tempered martensite.

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10.19 *Make a copy of the isothermal transformation diagram for an iron–carbon alloy of eutectoid composition (Figure 10.22) and then sketch and label time–temperature paths on this diagram to produce the following microstructures:*

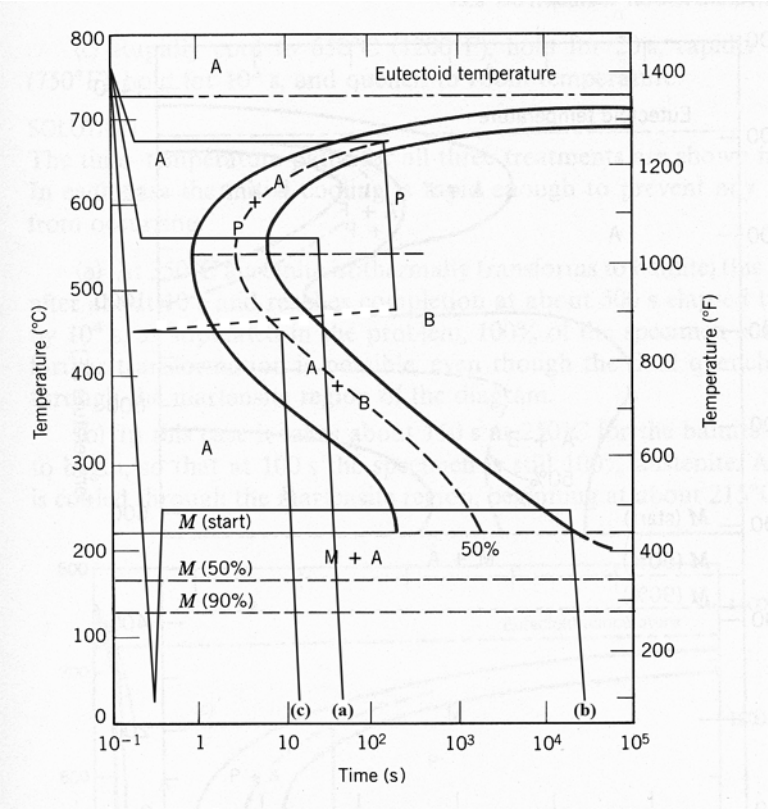
(a) 100% fine pearlite

(b) 100% tempered martensite

(c) 50% coarse pearlite, 25% bainite, and 25% martensite

Solution

Below is shown the isothermal transformation diagram for a eutectoid iron-carbon alloy, with time-temperature paths that will yield (a) 100% fine pearlite; (b) 100% tempered martensite; and (c) 50% coarse pearlite, 25% bainite, and 25% martensite.



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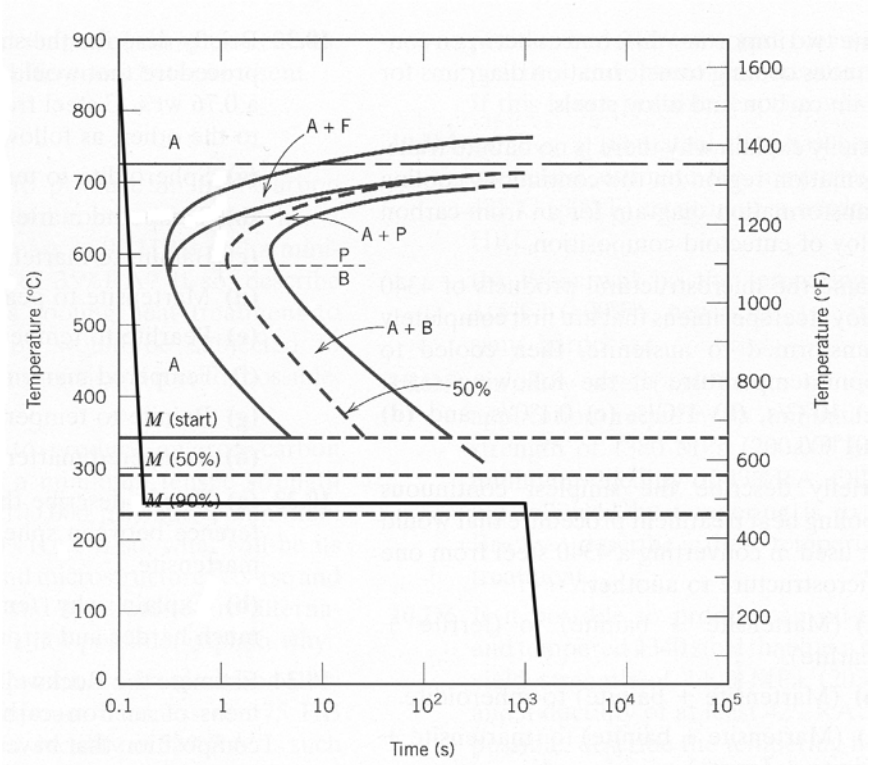
10.20 *Using the isothermal transformation diagram for a 0.45 wt% C steel alloy (Figure 10.39), determine the final microstructure (in terms of just the microconstituents present) of a small specimen that has been subjected to the following time-temperature treatments. In each case assume that the specimen begins at 845°C (1550°F), and that it has been held at this temperature long enough to have achieved a complete and homogeneous austenitic structure.*

(a) Rapidly cool to 250°C (480°F), hold for 10^3 s, then quench to room temperature.

Solution

Below is Figure 10.39 upon which is superimposed the above heat treatment.



While rapidly cooling to 250°C about 80% of the specimen transforms to martensite; during the 1000 s isothermal treatment at 250°C no additional transformations occur. During the final cooling to room temperature, the untransformed austenite also transforms to martensite. Hence, the final microstructure consists of 100% martensite.

(b) Rapidly cool to 700°C (1290°F), hold for 30 s, then quench to room temperature.

Solution

Below is Figure 10.39 upon which is superimposed the above heat treatment.

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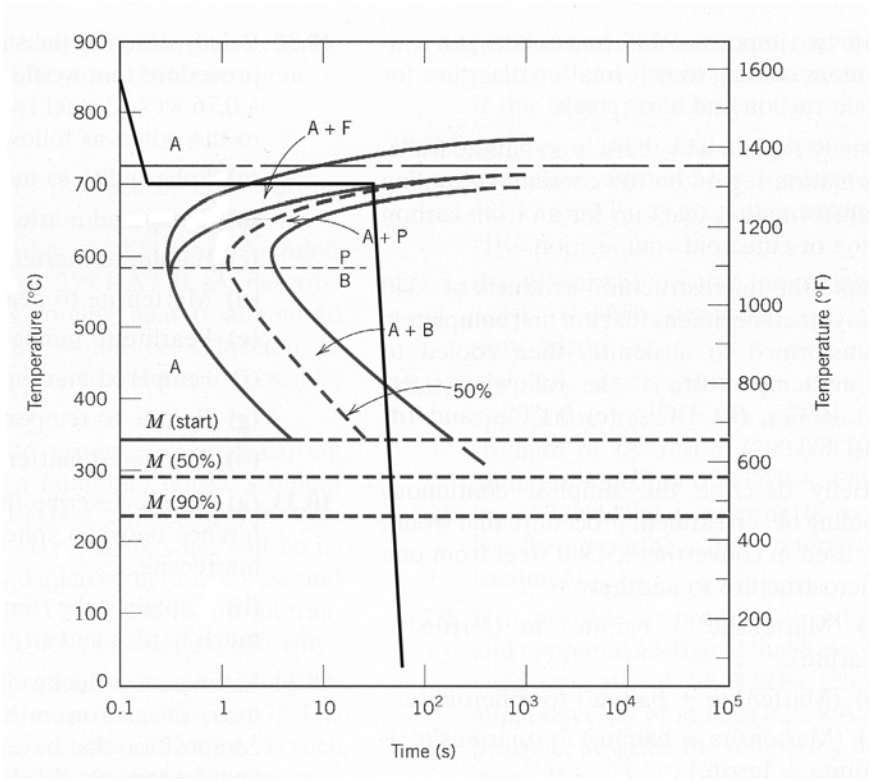

After cooling to and holding at 700°C for 30 s, a portion of specimen has transformed to proeutectoid ferrite. While cooling to room temperature, the remainder of the specimen transforms to martensite. Hence, the final microstructure consists proeutectoid ferrite and martensite.

(c) Rapidly cool to 400°C (750°F), hold for 500 s, then quench to room temperature.

Solution

Below is Figure 10.39 upon which is superimposed the above heat treatment.

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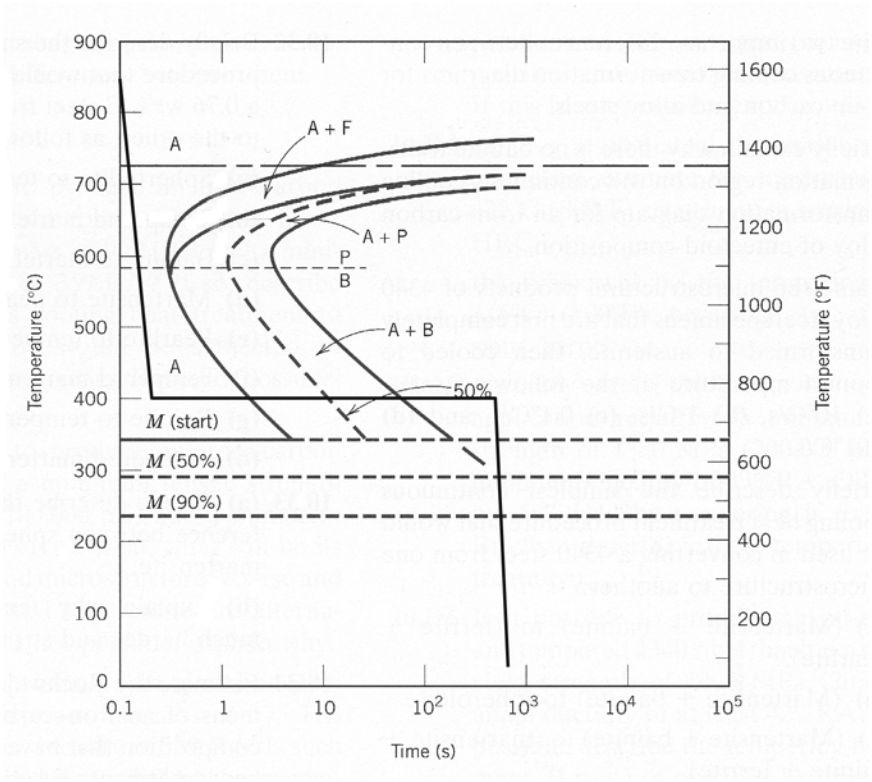

After cooling to and holding at 400°C for 500 s, all of the specimen has transformed to bainite. Hence, the final microstructure consists of 100% bainite.

(d) Rapidly cool to 700°C (1290°F), hold at this temperature for 10^5 s, then quench to room temperature.

Solution

Below is Figure 10.39 upon which is superimposed the above heat treatment.

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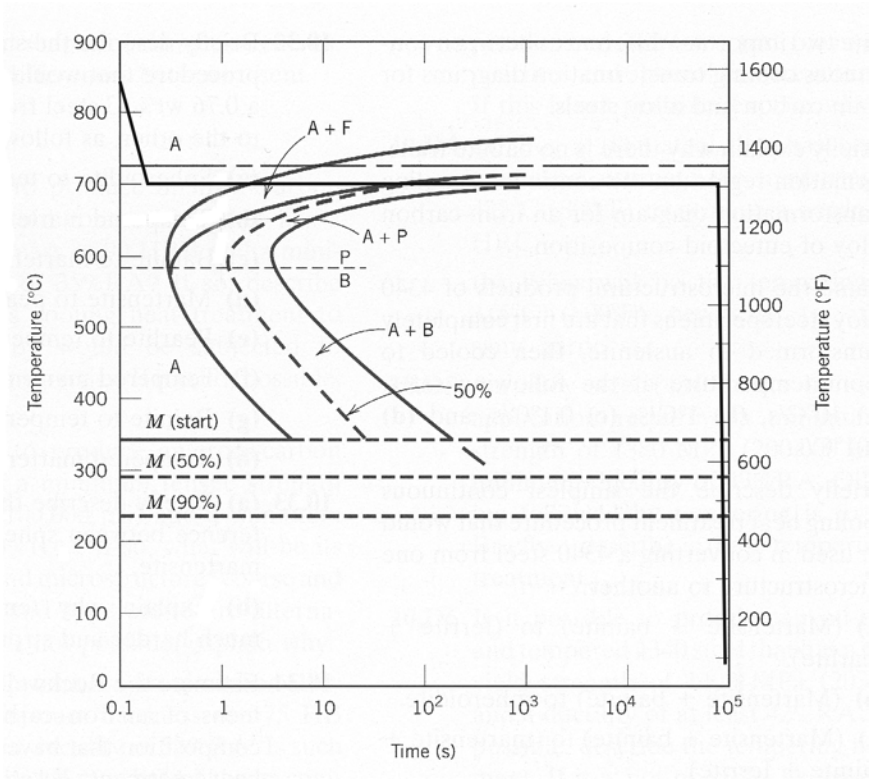

After cooling to and while holding at 700°C the specimen first transforms to proeutectoid ferrite and coarse pearlite. Continued heat treating at 700°C for 10^5 s results in a further transformation into spheroidite. Hence, the final microstructure consists of 100% spheroidite.

(e) Rapidly cool to 650°C (1200°F), hold at this temperature for 3 s, rapidly cool to 400°C (750°F), hold for 10 s, then quench to room temperature.

Solution

Below is Figure 10.39 upon which is superimposed the above heat treatment.

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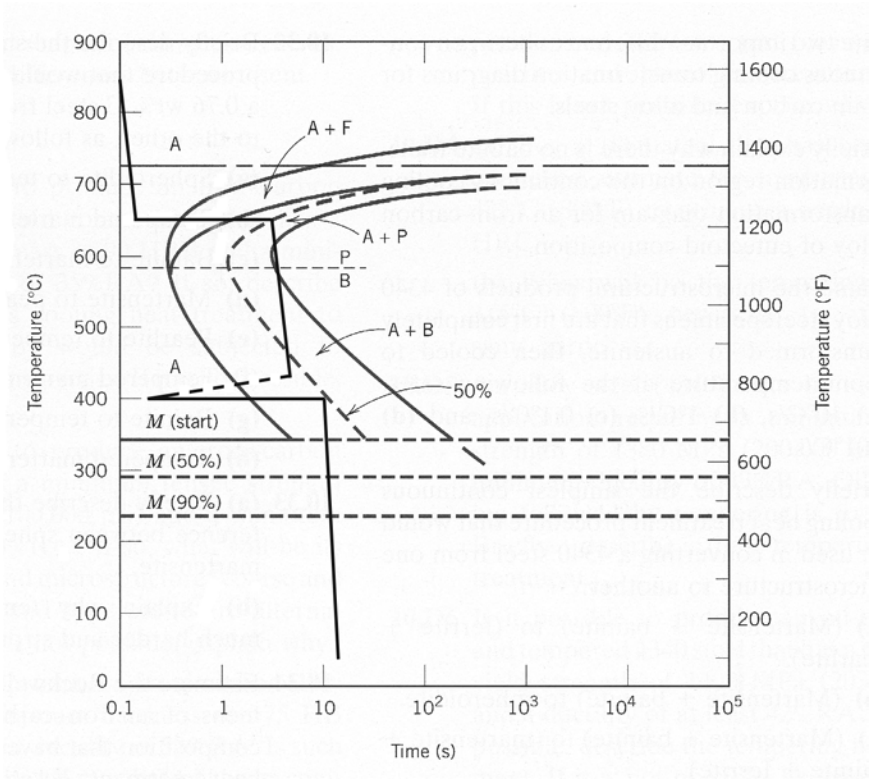

After cooling to and holding at 650°C for 3 s, some of the specimen first transformers to proeutectoid ferrite and then to pearlite (medium). During the second stage of the heat treatment at 400°C, some (but not all) of the remaining unreacted austenite transforms to bainite. As a result of the final quenching, all of the remaining austenite transforms to martensite. Hence, the final microstructure consists of ferrite, pearlite (medium), bainite, and martensite.

(f) Rapidly cool to 450°C (840°F), hold for 10 s, then quench to room temperature.

Solution

Below is Figure 10.39 upon which is superimposed the above heat treatment.

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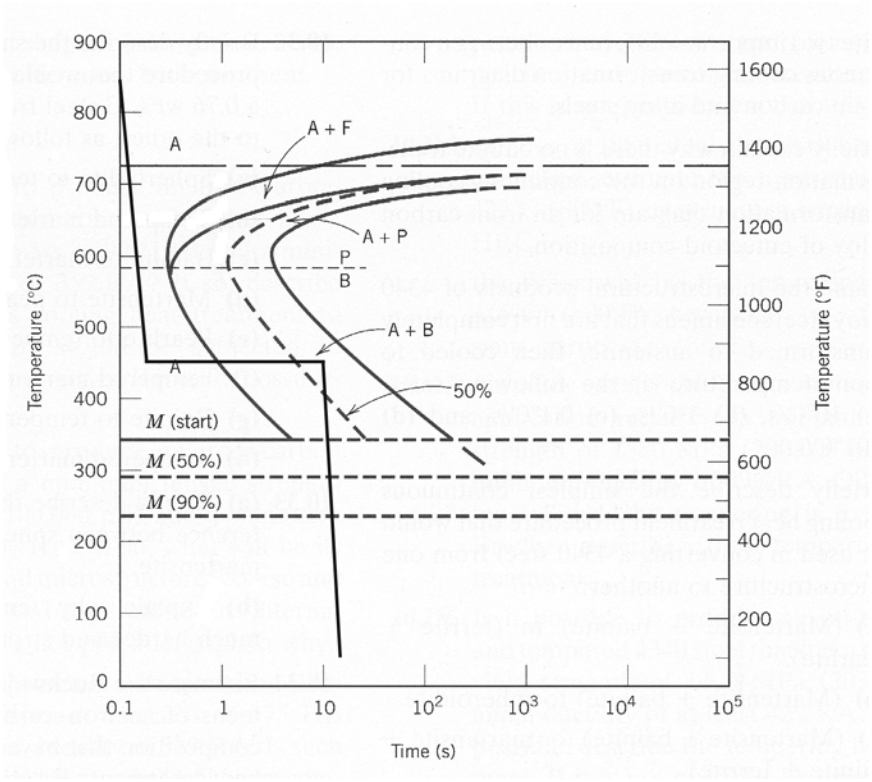

After cooling to and holding at 450°C for 10 s, a portion of the specimen first transformers to bainite. During the quenching to room temperature, the remainder of the specimen transforms to martensite. Hence, the final microstructure consists of bainite and martensite.

(g) Rapidly cool to 625°C (1155°F), hold for 1 s, then quench to room temperature.

Solution

Below is Figure 10.39 upon which is superimposed the above heat treatment.

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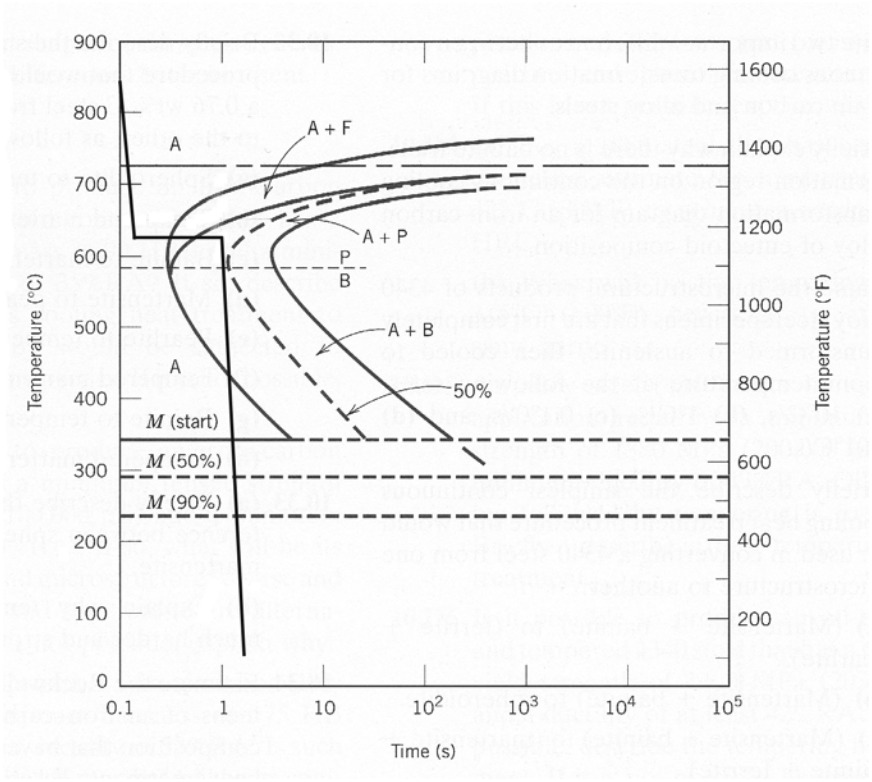

After cooling to and holding at 625°C for 1 s, a portion of the specimen first transformers to proeutectoid ferrite and pearlite. During the quenching to room temperature, the remainder of the specimen transforms to martensite. Hence, the final microstructure consists of ferrite, pearlite, and martensite.

(h) Rapidly cool to 625°C (1155°F), hold at this temperature for 10 s, rapidly cool to 400°C (750°F), hold at this temperature for 5 s, then quench to room temperature.

Solution

Below is Figure 10.39 upon which is superimposed the above heat treatment.

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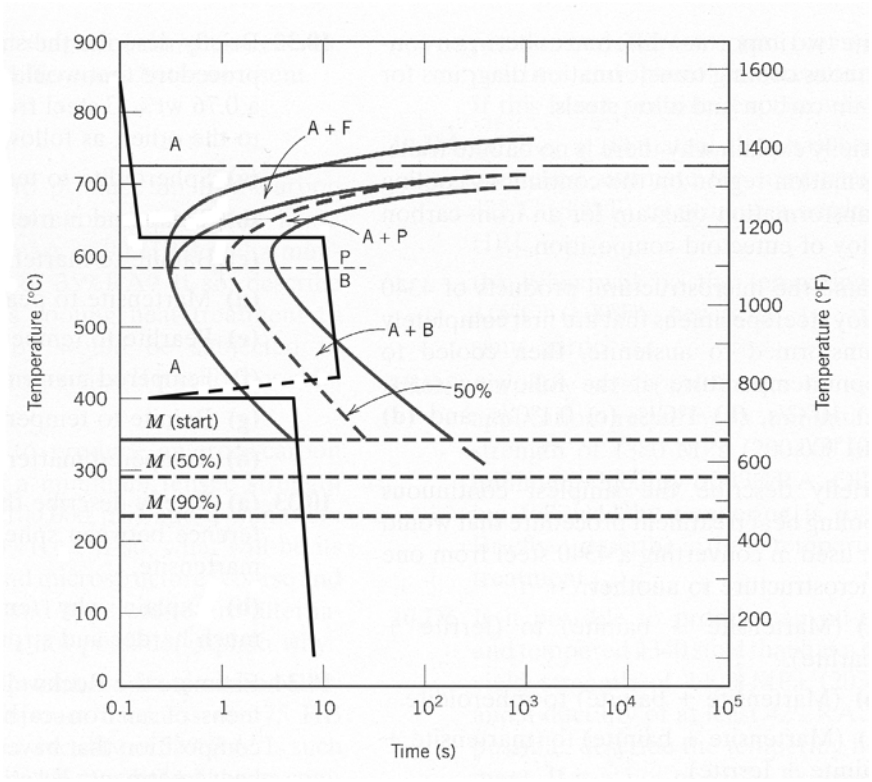

After cooling to and holding at 625°C for 10 s, all of the specimen transformers to proeutectoid ferrite and pearlite. During the second part of the heat treatment at 400°C no additional transformation will occur. Hence, the final microstructure consists of ferrite and pearlite.

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10.21 *For parts (a), (c), (d), (f), and (h) of Problem 10.20, determine the approximate percentages of the microconstituents that form.*

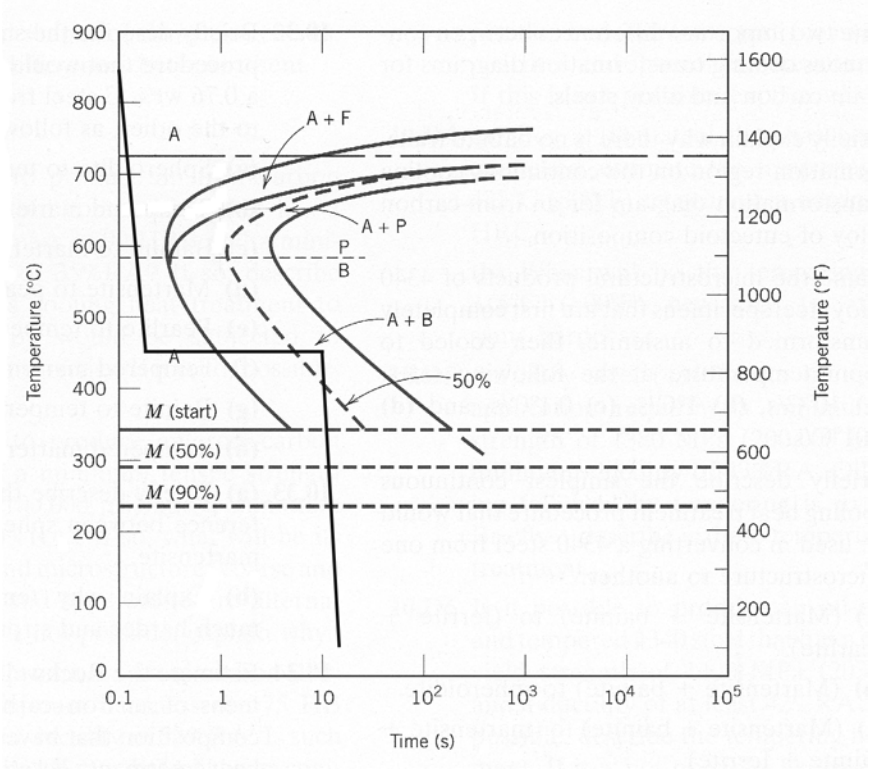
Solution

(a) From Problem 10.20(a) the microstructure consists of 100% martensite.

(c) From Problem 10.20(c) the microstructure consists of 100% bainite.

(d) From Problem 10.20(d) the microstructure consists of 100% spheroidite.

(f) Figure 10.39 onto which the heat treatment for Problem 10.20(f) has been constructed is shown below.



From this diagram, for the isothermal heat treatment at 450°C, the horizontal line constructed at this temperature and that ends at the 10 s point spans approximately 70% of the distance between the bainite reaction start and reaction completion curves. Therefore, the final microstructure consists of about 70% bainite and 30% martensite (the martensite forms while cooling to room temperature after 10 s at 450°C).

(h) Figure 10.39 onto which the heat treatment for Problem 10.20(h) has been constructed is shown below.

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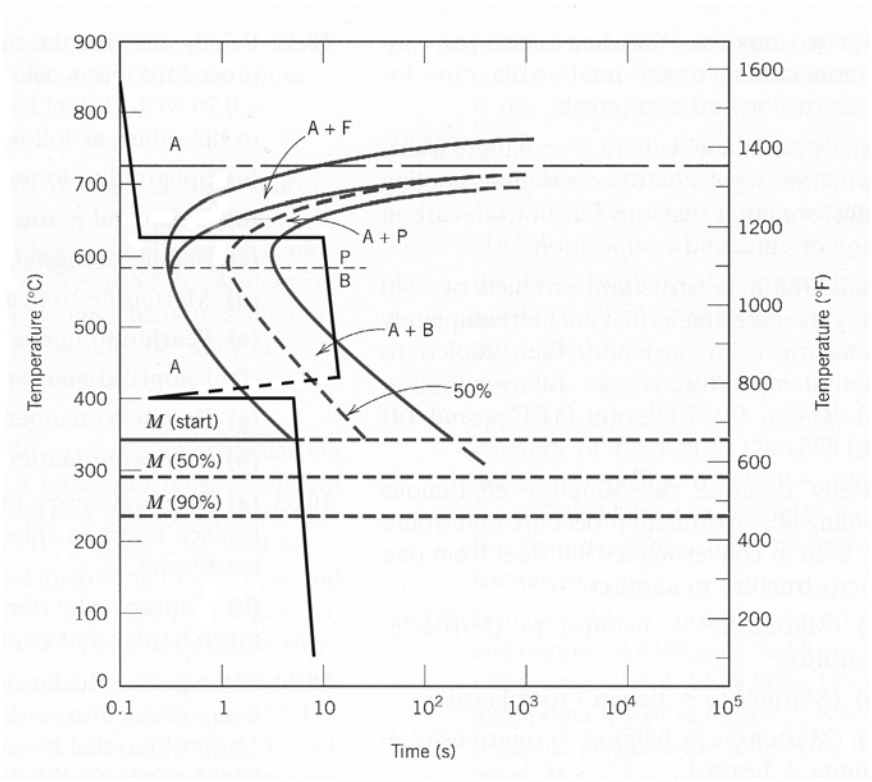

After holding for 10 s at 625°C, the specimen has completely transformed to proeutectoid ferrite and fine pearlite; no further reaction will occur at 400°C. Therefore, we can calculate the mass fractions using the appropriate lever rule expressions, Equations 9.20 and 9.21, as follows:

$$W_p = \frac{C_0' - 0.022}{0.74} = \frac{0.45 - 0.022}{0.74} = 0.58 \text{ or } 58\%$$

$$W_{\alpha'} = \frac{0.76 - C_0'}{0.74} = \frac{0.76 - 0.45}{0.74} = 0.42 \text{ or } 42\%$$

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10.22 *Make a copy of the isothermal transformation diagram for a 0.45 wt% C iron-carbon alloy (Figure 10.39), and then sketch and label on this diagram the time-temperature paths to produce the following microstructures:*

(a) 42% proeutectoid ferrite and 58% coarse pearlite

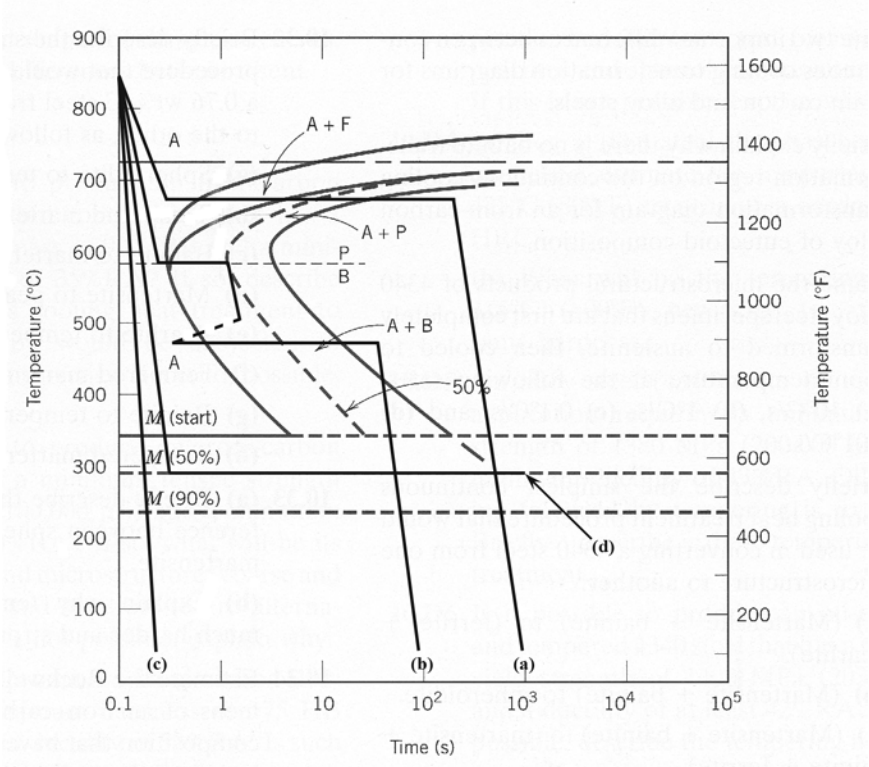
(b) 50% fine pearlite and 50% bainite

(c) 100% martensite

(d) 50% martensite and 50% austenite

Solution

Below is shown an isothermal transformation diagram for a 0.45 wt% C iron-carbon alloy, with time-temperature paths that will produce (a) 42% proeutectoid ferrite and 58% coarse pearlite; (b) 50% fine pearlite and 50% bainite; (c) 100% martensite; and (d) 50% martensite and 50% austenite.



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Continuous Cooling Transformation Diagrams

10.23 *Name the microstructural products of eutectoid iron–carbon alloy (0.76 wt% C) specimens that are first completely transformed to austenite, then cooled to room temperature at the following rates:*

(a) 200°C/s,

(b) 100°C/s, and

(c) 20°C/s.

Solution

We are called upon to name the microstructural products that form for specimens of an iron-carbon alloy of eutectoid composition that are continuously cooled to room temperature at a variety of rates. Figure 10.27 is used in these determinations.

(a) At a rate of 200°C/s, only martensite forms.

(b) At a rate of 100°C/s, both martensite and pearlite form.

(c) At a rate of 20°C/s, only fine pearlite forms.

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10.24 *Figure 10.40 shows the continuous cooling transformation diagram for a 1.13 wt% C iron-carbon alloy. Make a copy of this figure and then sketch and label continuous cooling curves to yield the following microstructures:*

(a) Fine pearlite and proeutectoid cementite

(b) Martensite

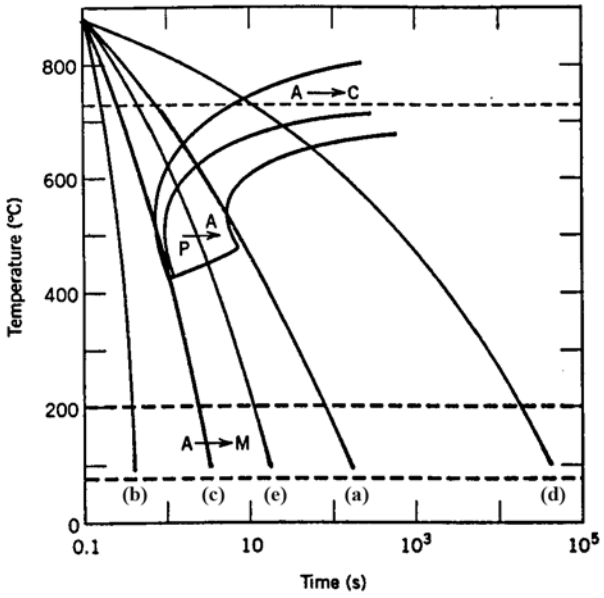
(c) Martensite and proeutectoid cementite

(d) Coarse pearlite and proeutectoid cementite

(e) Martensite, fine pearlite, and proeutectoid cementite

Solution

Below is shown a continuous cooling transformation diagram for a 1.13 wt% C iron-carbon alloy, with continuous cooling paths that will produce (a) fine pearlite and proeutectoid cementite; (b) martensite; (c) martensite and proeutectoid cementite; (d) coarse pearlite and proeutectoid cementite; and (e) martensite, fine pearlite, and proeutectoid cementite.



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10.25 *Cite two important differences between continuous cooling transformation diagrams for plain carbon and alloy steels.*

Solution

Two important differences between continuous cooling transformation diagrams for plain carbon and alloy steels are: (1) for an alloy steel, a bainite nose will be present, which nose will be absent for plain carbon alloys; and (2) the pearlite-proeutectoid noses for plain carbon steel alloys are positioned at shorter times than for the alloy steels.

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10.26 *Briefly explain why there is no bainite transformation region on the continuous cooling transformation diagram for an iron–carbon alloy of eutectoid composition.*

Solution

There is no bainite transformation region on the continuous cooling transformation diagram for an iron-carbon alloy of eutectoid composition (Figure 10.25) because by the time a cooling curve has passed into the bainite region, the entirety of the alloy specimen will have transformed to pearlite.

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10.27 *Name the microstructural products of 4340 alloy steel specimens that are first completely transformed to austenite, then cooled to room temperature at the following rates:*

(a) 10°C/s,

(b) 1°C/s,

(c) 0.1°C/s, and

(d) 0.01°C/s.

Solution

This problem asks for the microstructural products that form when specimens of a 4340 steel are continuously cooled to room temperature at several rates. Figure 10.28 is used for these determinations.

(a) At a cooling rate of 10°C/s, only martensite forms.

(b) At a cooling rate of 1°C/s, both martensite and bainite form.

(c) At a cooling rate of 0.1°C/s, martensite, proeutectoid ferrite, and bainite form.

(d) At a cooling rate of 0.01°C/s, martensite, proeutectoid ferrite, pearlite, and bainite form.

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10.28 *Briefly describe the simplest continuous cooling heat treatment procedure that would be used in converting a 4340 steel from one microstructure to another.*

(a) (Martensite + bainite) to (ferrite + pearlite)

(b) (Martensite + bainite) to spheroidite

(c) (Martensite + bainite) to (martensite + bainite + ferrite)

Solution

This problem asks that we briefly describe the simplest continuous cooling heat treatment procedure that would be used in converting a 4340 steel from one microstructure to another. Solutions to this problem require the use of Figure 10.28.

(a) In order to convert from (martensite + bainite) to (ferrite + pearlite) it is necessary to heat above about 720°C, allow complete austenitization, then cool to room temperature at a rate slower than 0.006°C/s.

(b) To convert from (martensite + bainite) to spheroidite the alloy must be heated to about 700°C for several hours.

(c) In order to convert from (martensite + bainite) to (martensite + bainite + ferrite) it is necessary to heat to above about 720°C, allow complete austenitization, then cool to room temperature at a rate between 0.3°C/s and 0.02°C/s.

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10.29 *On the basis of diffusion considerations, explain why fine pearlite forms for the moderate cooling of austenite through the eutectoid temperature, whereas coarse pearlite is the product for relatively slow cooling rates.*

Solution

For moderately rapid cooling, the time allowed for carbon diffusion is not as great as for slower cooling rates. Therefore, the diffusion distance is shorter, and thinner layers of ferrite and cementite form (i.e., fine pearlite forms).

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Mechanical Behavior of Iron-Carbon Alloys
Tempered Martensite

10.30 *Briefly explain why fine pearlite is harder and stronger than coarse pearlite, which in turn is harder and stronger than spheroidite.*

Solution

The hardness and strength of iron-carbon alloys that have microstructures consisting of α-ferrite and cementite phases depend on the boundary area between the two phases. The greater this area, the harder and stronger the alloy inasmuch as (1) these boundaries impede the motion of dislocations, and (2) the cementite phase restricts the deformation of the ferrite phase in regions adjacent to the phase boundaries. Fine pearlite is harder and stronger than coarse pearlite because the alternating ferrite-cementite layers are thinner for fine, and therefore, there is more phase boundary area. The phase boundary area between the sphere-like cementite particles and the ferrite matrix is less in spheroidite than for the alternating layered microstructure found in coarse pearlite.

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10.31 *Cite two reasons why martensite is so hard and brittle.*

Solution

Two reasons why martensite is so hard and brittle are: (1) there are relatively few operable slip systems for the body-centered tetragonal crystal structure, and (2) virtually all of the carbon is in solid solution, which produces a solid-solution hardening effect.

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10.32 *Rank the following iron–carbon alloys and associated microstructures from the highest to the lowest tensile strength:*

(a) 0.25 wt%C with spheroidite,

(b) 0.25 wt%C with coarse pearlite,

(c) 0.60 wt%C with fine pearlite, and

(d) 0.60 wt%C with coarse pearlite.

Justify this ranking.

Solution

This problem asks us to rank four iron-carbon alloys of specified composition and microstructure according to hardness. This ranking is as follows:

0.60 wt% C, fine pearlite
0.60 wt% C, coarse pearlite
0.25 wt% C, coarse pearlite
0.25 wt% C, spheroidite

The 0.25 wt% C, coarse pearlite is stronger than the 0.25 wt% C, spheroidite since coarse pearlite is stronger than spheroidite; the composition of the alloys is the same. The 0.60 wt% C, coarse pearlite is stronger than the 0.25 wt% C, coarse pearlite, since increasing the carbon content increases the strength. Finally, the 0.60 wt% C, fine pearlite is stronger than the 0.60 wt% C, coarse pearlite inasmuch as the strength of fine pearlite is greater than coarse pearlite because of the many more ferrite-cementite phase boundaries in fine pearlite.

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10.33 *Briefly explain why the hardness of tempered martensite diminishes with tempering time (at constant temperature) and with increasing temperature (at constant tempering time).*

Solution

This question asks for an explanation as to why the hardness of tempered martensite diminishes with tempering time (at constant temperature) and with increasing temperature (at constant tempering time). The hardness of tempered martensite depends on the ferrite-cementite phase boundary area; since these phase boundaries are barriers to dislocation motion, the greater the area the harder the alloy. The microstructure of tempered martensite consists of small sphere-like particles of cementite embedded within a ferrite matrix. As the size of the cementite particles increases, the phase boundary area diminishes, and the alloy becomes softer. Therefore, with increasing tempering time, the cementite particles grow, the phase boundary area decreases, and the hardness diminishes. As the tempering temperature is increased, the rate of cementite particle growth also increases, and the alloy softens, again, because of the decrease in phase boundary area.

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10.34 *Briefly describe the simplest heat treatment procedure that would be used in converting a 0.76 wt% C steel from one microstructure to the other, as follows:*

(a) Spheroidite to tempered martensite

(b) Tempered martensite to pearlite

(c) Bainite to martensite

(d) Martensite to pearlite

(e) Pearlite to tempered martensite

(f) Tempered martensite to pearlite

(g) Bainite to tempered martensite

(h) Tempered martensite to spheroidite

Solution

In this problem we are asked to describe the simplest heat treatment that would be required to convert a eutectoid steel from one microstructure to another. Figure 10.27 is used to solve the several parts of this problem.

(a) For spheroidite to tempered martensite, austenitize at a temperature of about 760°C, quench to room temperature at a rate greater than about 140°C/s, then isothermally heat at a temperature between 250 and 650°C.

(b) For tempered martensite to pearlite, austenitize at a temperature of about 760°C, then cool to room temperature at a rate less than about 35°C/s.

(c) For bainite to martensite, first austenitize at a temperature of about 760°C, then quench to room temperature at a rate greater than about 140°C/s.

(d) For martensite to pearlite, first austenitize at a temperature of about 760°C, then cool to room temperature at a rate less than about 35°C/s.

(e) For pearlite to tempered martensite, first austenitize at a temperature of about 760°C, then rapidly quench to room temperature at a rate greater than about 140°C/s, then isothermally heat treat (temper) at a temperature between 250 and 650°C.

(f) For tempered martensite to pearlite, first austenitize at a temperature of about 760°C, then cool to room temperature at a rate less than about 35°C/s.

(g) For bainite to tempered martensite, first austenitize at a temperature of about 760°C, then rapidly quench to room temperature at a rate greater than about 140°C/s, then isothermally heat treat (temper) at a temperature between 250 and 650°C.

(h) For tempered martensite to spheroidite simply heat at about 700°C for approximately 20 h.

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10.35 *(a) Briefly describe the microstructural difference between spheroidite and tempered martensite.*

(b) Explain why tempered martensite is much harder and stronger.

Solution

(a) Both tempered martensite and spheroidite have sphere-like cementite particles within a ferrite matrix; however, these particles are much larger for spheroidite.

(b) Tempered martensite is harder and stronger inasmuch as there is much more ferrite-cementite phase boundary area for the smaller particles; thus, there is greater reinforcement of the ferrite phase, and more phase boundary barriers to dislocation motion.

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10.36 *Estimate the Rockwell hardnesses for specimens of an iron–carbon alloy of eutectoid composition that have been subjected to the heat treatments described in parts (b), (d), (f), (g), and (h) of Problem 10.18.*

Solution

This problem asks for estimates of Rockwell hardness values for specimens of an iron-carbon alloy of eutectoid composition that have been subjected to some of the heat treatments described in Problem 10.18.

(b) The microstructural product of this heat treatment is 100% spheroidite. According to Figure 10.30*a*, the hardness of a 0.76 wt% C alloy with spheroidite is about 87 HRB.

(d) The microstructural product of this heat treatment is 100% martensite. According to Figure 10.32, the hardness of a 0.76 wt% C alloy consisting of martensite is about 64 HRC.

(f) The microstructural product of this heat treatment is 100% bainite. From Figure 10.31, the hardness of a 0.76 wt% C alloy consisting of bainite is about 385 HB. And, conversion from Brinell to Rockwell hardness using Figure 6.18 leads to a hardness of 36 HRC.

(g) The microstructural product of this heat treatment is 100% fine pearlite. According to Figure 10.30*a*, the hardness of a 0.76 wt% C alloy consisting of fine pearlite is about 27 HRC.

(h) The microstructural product of this heat treatment is 100% tempered martensite. According to Figure 10.35, the hardness of a water-quenched eutectoid alloy that was tempered at 315°C for one hour is about 57 HRC.

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10.37 *Estimate the Brinell hardnesses for specimens of a 0.45 wt% C iron-carbon alloy that have been subjected to the heat treatments described in parts (a), (d), and (h) of Problem 10.20.*

Solution

This problem asks for estimates of Brinell hardness values for specimens of an iron-carbon alloy of composition 0.45 wt% C that have been subjected to some of the heat treatments described in Problem 10.20.

(a) The microstructural product of this heat treatment is 100% martensite. According to Figure 10.32, the hardness of a 0.45 wt% C alloy consisting of martensite is about 630 HB.

(d) The microstructural product of this heat treatment is 100% spheroidite. According to Figure 10.30*a* the hardness of a 0.45 wt% C alloy with spheroidite is about 150 HB.

(h) The microstructural product of this heat treatment is proeutectoid ferrite and fine pearlite. According to Figure 10.30*a*, the hardness of a 0.45 wt% C alloy consisting of fine pearlite is about 200 HB.

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10.38 *Determine the approximate tensile strengths for specimens of a eutectoid iron–carbon alloy that have experienced the heat treatments described in parts (a) and (c) of Problem 10.23.*

Solution

This problem asks for estimates of tensile strength values for specimens of an iron-carbon alloy of eutectoid composition that have been subjected to some of the heat treatments described in Problem 10.23.

(a) The microstructural product of this heat treatment is 100% martensite. According to Figure 10.32, the hardness of a 0.76 wt% C alloy is about 690 HB. For steel alloys, hardness and tensile strength are related through Equation 6.20a, and therefore

$$TS\,(\text{MPa}) = 3.45 \times \text{HB} = (3.45)(690\ \text{HB}) = 2380\ \text{MPa} \quad (345{,}000\ \text{psi})$$

(c) The microstructural product of this heat treatment is 100% fine pearlite. According to Figure 10.30*a*, the hardness of a 0.76 wt% C alloy consisting of fine pearlite is about 265 HB. Therefore, the tensile strength is

$$TS\,(\text{MPa}) = 3.45 \times \text{HB} = (3.45)(265\ \text{HB}) = 915\ \text{MPa} \quad (132{,}500\ \text{psi})$$

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10.39 *For a eutectoid steel, describe isothermal heat treatments that would be required to yield specimens having the following Rockwell hardnesses:*

(a) 93 HRB,

(b) 40 HRC, and

(c) 27 HRC.

Solution

For this problem we are asked to describe isothermal heat treatments required to yield specimens having several Brinell hardnesses.

(a) From Figure 10.30*a*, in order for a 0.76 wt% C alloy to have a Rockwell hardness of 93 HRB, the microstructure must be coarse pearlite. Thus, utilizing the isothermal transformation diagram for this alloy, Figure 10.22, we must rapidly cool to a temperature at which coarse pearlite forms (i.e., to about 675°C), allow the specimen to isothermally and completely transform to coarse pearlite. At this temperature an isothermal heat treatment for at least 200 s is required.

(b) This portion of the problem asks for a hardness of 40 HRC the microstructure could consist of either (1) about 75% fine pearlite and 25% martensite (Figure 10.32), or (2) tempered martensite (Figure 10.35).

For case (1), after austenitizing, rapidly cool to about 580°C (Figure 10.22), hold at this temperature for about 4 s (to obtain 75% fine pearlite), and then rapidly quench to room temperature.

For case (2), after austenitizing, rapidly cool to room temperature in order to achieve 100% martensite. Then temper this martensite for about 2000 s at 535°C (Figure 10.35).

(c) From Figure 10.30*a*, in order for a 0.76 wt% C alloy to have a Rockwell hardness of 27 HRC, the microstructure must be fine pearlite. Thus, utilizing the isothermal transformation diagram for this alloy, Figure 10.22, we must rapidly cool to a temperature at which fine pearlite forms (i.e., at about 580°C), allow the specimen to isothermally and completely transform to fine pearlite. At this temperature an isothermal heat treatment for at least 7 s is required.

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DESIGN PROBLEMS

Continuous Cooling Transformation Diagrams
Mechanical Behavior of Iron-Carbon Alloys

10.D1 *Is it possible to produce an iron-carbon alloy of eutectoid composition that has a minimum hardness of 90 HRB and a minimum ductility of 35%RA? If so, describe the continuous cooling heat treatment to which the alloy would be subjected to achieve these properties. If it is not possible, explain why.*

Solution

This problem inquires as to the possibility of producing an iron-carbon alloy of eutectoid composition that has a minimum hardness of 90 HRB and a minimum ductility of 35%RA. If the alloy is possible, then the continuous cooling heat treatment is to be stipulated.

According to Figures 10.30*a* and *b*, the following is a tabulation of Rockwell B hardnesses and percents area reduction for fine and coarse pearlites and spheroidite for a 0.76 wt% C alloy.

Microstructure	HRB	%RA
Fine pearlite	> 100	20
Coarse pearlite	93	28
Spheroidite	88	67

Therefore, none of the microstructures meets both of these criteria. Both fine and coarse pearlites are hard enough, but lack the required ductility. Spheroidite is sufficiently ductile, but does not meet the hardness criterion.

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10.D2 *Is it possible to produce an iron-carbon alloy that has a minimum tensile strength of 690 MPa (100,000 psi) and a minimum ductility of 40%RA? If so, what will be its composition and microstructure (coarse and fine pearlites and spheroidite are alternatives)? If this is not possible, explain why.*

Solution

This problem asks if it is possible to produce an iron-carbon alloy that has a minimum tensile strength of 690 MPa (100,000 psi) and a minimum ductility of 40%RA. If such an alloy is possible, its composition and microstructure are to be stipulated.

From Equation 6.20a, this tensile strength corresponds to a Brinell hardness of

$$\text{HB} = \frac{TS\ (\text{MPa})}{3.45} = \frac{690\ \text{MPa}}{3.45} = 200$$

According to Figures 10.30*a* and *b*, the following is a tabulation of the composition ranges for fine and coarse pearlites and spheroidite that meet the stipulated criteria.

Microstructure	Compositions for HB ≥ 200	Compositions for %RA ≥ 40%
Fine pearlite	> 0.45 %C	< 0.47 %C
Coarse pearlite	> 0.7 %C	< 0.54 %C
Spheroidite	not possible	0-1.0 %C

Therefore, only fine pearlite has a composition range overlap for both of the hardness and ductility restrictions; the fine pearlite would necessarily have to have a carbon content between 0.45 and 0.47 wt% C.

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10.D3 *It is desired to produce an iron-carbon alloy that has a minimum hardness of 175 HB and a minimum ductility of 52%RA. Is such an alloy possible? If so, what will be its composition and microstructure (coarse and fine pearlites and spheroidite are alternatives)? If this is not possible, explain why.*

Solution

This problem inquires as to the possibility of producing a iron-carbon alloy having a minimum hardness of 175 HB and a minimum ductility of 52%RA. The composition and microstructure are to be specified; possible microstructures include fine and coarse pearlites and spheroidite.

To solve this problem, we must consult Figures 10.30*a* and *b*. The following is a tabulation of the composition ranges for fine and coarse pearlites and spheroidite that meet the stipulated criteria.

Microstructure	Compositions for HB ≥ 175	Compositions for %RA ≥ 52%
Fine pearlite	> 0.36 %C	< 0.33 %C
Coarse pearlite	> 0.43 %C	< 0.40 %C
Spheroidite	> 0.70	<0-1.0 %C

Thus, only spheroidite has a composition overlap for both of hardness and ductility restrictions; the spheroidite would necessarily have to have a carbon content greater than 0.70 wt% C.

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Tempered Martensite

10.D4 *(a) For a 1080 steel that has been water quenched, estimate the tempering time at 425°C (800°F) to achieve a hardness of 50 HRC.*

(b) What will be the tempering time at 315°C (600°F) necessary to attain the same hardness?

Solution

This problem asks us to consider the tempering of a water-quenched 1080 steel to achieve a hardness of 50 HRC. It is necessary to use Figure 10.35.

(a) The time necessary at 425°C is about 500 s.

(b) At 315°C, the time required (by extrapolation) is approximately 4×10^6 s (about 50 days).

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10.D5 *An alloy steel (4340) is to be used in an application requiring a minimum tensile strength of 1380 MPa (200,000 psi) and a minimum ductility of 43%RA. Oil quenching followed by tempering is to be used. Briefly describe the tempering heat treatment.*

Solution

We are to consider the tempering of an oil-quenched 4340 steel. From Figure 10.34, for a minimum tensile strength of 1380 MPa (200,000 psi) a tempering temperature of less than 450°C (840°F) is required. Also, for a minimum ductility of 43%RA, tempering must be carried out at a temperature greater than about 400°C (750°F). Therefore, tempering must occur at between 400 and 450°C (750 and 840°F) for 1 h.

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10.D6 *Is it possible to produce an oil-quenched and tempered 4340 steel that has a minimum yield strength of 1400 MPa (203,000 psi) and a ductility of at least 42%RA? If this is possible, describe the tempering heat treatment. If it is not possible, explain why.*

Solution

This problem asks if it is possible to produce an oil-quenched and tempered 4340 steel that has a minimum yield strength of 1400 MPa (203,000 psi) and a minimum ductility of 42%RA, and, if possible, to describe the tempering heat treatment. In Figure 10.34 is shown the tempering characteristics of this alloy. According to this figure, in order to achieve a minimum yield strength of 1400 MPa a tempering temperature of less that about 410°C is required. On the other hand, tempering must be carried out at greater than about 360°C for a minimum ductility of 42%RA. Therefore, an oil-quenched and tempered 4340 alloy possessing these characteristics is possible; tempering would be carried out at between 360°C and 410°C for 1 h.

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CHAPTER 11

APPLICATIONS AND PROCESSING OF METAL ALLOYS

PROBLEM SOLUTIONS

Ferrous Alloys

11.1 *(a) List the four classifications of steels. (b) For each, briefly describe the properties and typical applications.*

Solution

This question asks that we list four classifications of steels, and, for each, to describe properties and cite typical applications.

Low Carbon Steels

Properties: nonresponsive to heat treatments; relatively soft and weak; machinable and weldable.

Typical applications: automobile bodies, structural shapes, pipelines, buildings, bridges, and tin cans.

Medium Carbon Steels

Properties: heat treatable, relatively large combinations of mechanical characteristics.

Typical applications: railway wheels and tracks, gears, crankshafts, and machine parts.

High Carbon Steels

Properties: hard, strong, and relatively brittle.

Typical applications: chisels, hammers, knives, and hacksaw blades.

High Alloy Steels (Stainless and Tool)

Properties: hard and wear resistant; resistant to corrosion in a large variety of environments.

Typical applications: cutting tools, drills, cutlery, food processing, and surgical tools.

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11.2 *(a) Cite three reasons why ferrous alloys are used so extensively. (b) Cite three characteristics of ferrous alloys that limit their utilization.*

Solution

(a) Ferrous alloys are used extensively because:

(1) Iron ores exist in abundant quantities.

(2) Economical extraction, refining, and fabrication techniques are available.

(3) The alloys may be tailored to have a wide range of properties.

(b) Disadvantages of ferrous alloys are:

(1) They are susceptible to corrosion.

(2) They have a relatively high density.

(3) They have relatively low electrical conductivities.

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11.3 *What is the function of alloying elements in tool steels?*

Solution

The alloying elements in tool steels (e.g., Cr, V, W, and Mo) combine with the carbon to form very hard and wear-resistant carbide compounds.

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11.4 *Compute the volume percent of graphite V_{Gr} in a 3.5 wt% C cast iron, assuming that all the carbon exists as the graphite phase. Assume densities of 7.9 and 2.3 g/cm^3 for ferrite and graphite, respectively.*

Solution

We are asked to compute the volume percent graphite in a 3.5 wt% C cast iron. It first becomes necessary to compute mass fractions using the lever rule. From the iron-carbon phase diagram (Figure 11.2), the tie-line in the α and graphite phase field extends from essentially 0 wt% C to 100 wt% C. Thus, for a 3.5 wt% C cast iron

$$W_\alpha = \frac{C_{Gr} - C_0}{C_{Gr} - C_\alpha} = \frac{100 - 3.5}{100 - 0} = 0.965$$

$$W_{Gr} = \frac{C_0 - C_\alpha}{C_{Gr} - C_\alpha} = \frac{3.5 - 0}{100 - 0} = 0.035$$

Conversion from weight fraction to volume fraction of graphite is possible using Equation 9.6a as

$$V_{Gr} = \frac{\dfrac{W_{Gr}}{\rho_{Gr}}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_{Gr}}{\rho_{Gr}}}$$

$$= \frac{\dfrac{0.035}{2.3\ \text{g/cm}^3}}{\dfrac{0.965}{7.9\ \text{g/cm}^3} + \dfrac{0.035}{2.3\ \text{g/cm}^3}}$$

$$= 0.111 \text{ or } 11.1 \text{ vol\%}$$

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11.5 *On the basis of microstructure, briefly explain why gray iron is brittle and weak in tension.*

Solution

Gray iron is weak and brittle in tension because the tips of the graphite flakes act as points of stress concentration.

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11.6 *Compare gray and malleable cast irons with respect to (a) composition and heat treatment, (b) microstructure, and (c) mechanical characteristics.*

Solution

This question asks us to compare various aspects of gray and malleable cast irons.

(a) With respect to composition and heat treatment:

Gray iron--2.5 to 4.0 wt% C and 1.0 to 3.0 wt% Si. For most gray irons there is no heat treatment after solidification.

Malleable iron--2.5 to 4.0 wt% C and less than 1.0 wt% Si. White iron is heated in a nonoxidizing atmosphere and at a temperature between 800 and 900°C for an extended time period.

(b) With respect to microstructure:

Gray iron--Graphite flakes are embedded in a ferrite or pearlite matrix.

Malleable iron--Graphite clusters are embedded in a ferrite or pearlite matrix.

(c) With respect to mechanical characteristics:

Gray iron--Relatively weak and brittle in tension; good capacity for damping vibrations.

Malleable iron--Moderate strength and ductility.

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11.7 *Compare white and nodular cast irons with respect to (a) composition and heat treatment, (b) microstructure, and (c) mechanical characteristics.*

Solution

This question asks us to compare white and nodular cast irons.

(a) With regard to composition and heat treatment:

White iron--2.5 to 4.0 wt% C and less than 1.0 wt% Si. No heat treatment; however, cooling is rapid during solidification.

Nodular cast iron--2.5 to 4.0 wt% C, 1.0 to 3.0 wt% Si, and a small amount of Mg or Ce. A heat treatment at about 700°C may be necessary to produce a ferritic matrix.

(b) With regard to microstructure:

White iron--There are regions of cementite interspersed within pearlite.

Nodular cast iron--Nodules of graphite are embedded in a ferrite or pearlite matrix.

(c) With respect to mechanical characteristics:

White iron--Extremely hard and brittle.

Nodular cast iron--Moderate strength and ductility.

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11.8 *Is it possible to produce malleable cast iron in pieces having large cross-sectional dimensions? Why or why not?*

Solution

It is *not possible* to produce malleable iron in pieces having large cross-sectional dimensions. White cast iron is the precursor of malleable iron, and a rapid cooling rate is necessary for the formation of white iron, which may not be accomplished at interior regions of thick cross-sections.

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Nonferrous Alloys

11.9 *What is the principal difference between wrought and cast alloys?*

Solution

The principal difference between wrought and cast alloys is as follows: wrought alloys are ductile enough so as to be hot or cold worked during fabrication, whereas cast alloys are brittle to the degree that shaping by deformation is not possible and they must be fabricated by casting.

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11.10 *Why must rivets of a 2017 aluminum alloy be refrigerated before they are used?*

Solution

Rivets of a 2017 aluminum alloy must be refrigerated before they are used because, after being solution heat treated, they precipitation harden at room temperature. Once precipitation hardened, they are too strong and brittle to be driven.

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11.11 *What is the chief difference between heat-treatable and non-heat-treatable alloys?*

Solution

The chief difference between heat-treatable and nonheat-treatable alloys is that heat-treatable alloys may be strengthened by a heat treatment wherein a precipitate phase is formed (precipitation hardening) or a martensitic transformation occurs. Nonheat-treatable alloys are not amenable to strengthening by such treatments.

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11.12 *Give the distinctive features, limitations, and applications of the following alloy groups: titanium alloys, refractory metals, superalloys, and noble metals.*

Solution

Titanium Alloys

Distinctive features: relatively low density, high melting temperatures, and high strengths are possible.

Limitation: because of chemical reactivity with other materials at elevated temperatures, these alloys are expensive to refine.

Applications: aircraft structures, space vehicles, and in chemical and petroleum industries.

Refractory Metals

Distinctive features: extremely high melting temperatures; large elastic moduli, hardnesses, and strengths.

Limitation: some experience rapid oxidation at elevated temperatures.

Applications: extrusion dies, structural parts in space vehicles, incandescent light filaments, x-ray tubes, and welding electrodes.

Superalloys

Distinctive features: able to withstand high temperatures and oxidizing atmospheres for long time periods.

Applications: aircraft turbines, nuclear reactors, and petrochemical equipment.

Noble Metals

Distinctive features: highly resistant to oxidation, especially at elevated temperatures; soft and ductile.

Limitation: expensive.

Applications: jewelry, dental restoration materials, coins, catalysts, and thermocouples.

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Forming Operations

11.13 *Cite advantages and disadvantages of hot working and cold working.*

Solution

The advantages of cold working are:

(1) A high quality surface finish.

(2) The mechanical properties may be varied.

(3) Close dimensional tolerances.

The disadvantages of cold working are:

(1) High deformation energy requirements.

(2) Large deformations must be accomplished in steps, which may be expensive.

(3) A loss of ductility.

The advantages of hot working are:

(1) Large deformations are possible, which may be repeated.

(2) Deformation energy requirements are relatively low.

The disadvantages of hot working are:

(1) A poor surface finish.

(2) A variety of mechanical properties is not possible.

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11.14 *(a) Cite advantages of forming metals by extrusion as opposed to rolling. (b) Cite some disadvantages.*

Solution

(a) The advantages of extrusion as opposed to rolling are as follows:

(1) Pieces having more complicated cross-sectional geometries may be formed.

(2) Seamless tubing may be produced.

(b) The disadvantages of extrusion over rolling are as follows:

(1) Nonuniform deformation over the cross-section.

(2) A variation in properties may result over a cross-section of an extruded piece.

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Casting

11.15 *List four situations in which casting is the preferred fabrication technique.*

Solution

Four situations in which casting is the preferred fabrication technique are:

(1) For large pieces and/or complicated shapes.

(2) When mechanical strength is not an important consideration.

(3) For alloys having low ductilities.

(4) When it is the most economical fabrication technique.

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11.16 *Compare sand, die, investment, lost foam, and continuous casting techniques.*

Solution

For *sand casting*, sand is the mold material, a two-piece mold is used, ordinarily the surface finish is not an important consideration, the sand may be reused (but the mold may not), casting rates are low, and large pieces are usually cast.

For *die casting*, a permanent mold is used, casting rates are high, the molten metal is forced into the mold under pressure, a two-piece mold is used, and small pieces are normally cast.

For *investment casting*, a single-piece mold is used, which is not reusable; it results in high dimensional accuracy, good reproduction of detail, and a fine surface finish; and casting rates are low.

For *lost foam casting*, the pattern is polystyrene foam, whereas the mold material is sand. Complex geometries and tight tolerances are possible. Casting rates are higher than for investment, and there are few environmental wastes.

For *continuous casting*, at the conclusion of the extraction process, the molten metal is cast into a continuous strand having either a rectangular or circular cross-section; these shapes are desirable for subsequent secondary metal-forming operations. The chemical composition and mechanical properties are relatively uniform throughout the cross-section.

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Miscellaneous Techniques

11.17 *If it is assumed that, for steel alloys, the average cooling rate of the heat-affected zone in the vicinity of a weld is 10°C/s, compare the microstructures and associated properties that will result for 1080 (eutectoid) and 4340 alloys in their HAZs.*

Solution

This problem asks that we specify and compare the microstructures and mechanical properties in the heat-affected weld zones for 1080 and 4340 alloys assuming that the average cooling rate is 10°C/s. Figure 10.27 shows the continuous cooling transformation diagram for an iron-carbon alloy of eutectoid composition (1080), and, in addition, cooling curves that delineate changes in microstructure. For a cooling rate of 10°C/s (which is less than 35°C/s) the resulting microstructure will be totally pearlite--probably a reasonably fine pearlite. On the other hand, in Figure 10.28 is shown the CCT diagram for a 4340 steel. From this diagram it may be noted that a cooling rate of 10°C/s produces a totally martensitic structure. Pearlite is softer and more ductile than martensite, and, therefore, is most likely more desirable.

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11.18 *Describe one problem that might exist with a steel weld that was cooled very rapidly.*

Solution

If a steel weld is cooled very rapidly, martensite may form, which is very brittle. In some situations, cracks may form in the weld region as it cools.

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Annealing Processes

11.19 *In your own words describe the following heat treatment procedures for steels and, for each, the intended final microstructure: full annealing, normalizing, quenching, and tempering.*

Solution

Full annealing--Heat to about 50°C above the A_3 line, Figure 11.10 (if the concentration of carbon is less than the eutectoid) or above the A_1 line (if the concentration of carbon is greater than the eutectoid) until the alloy comes to equilibrium; then furnace cool to room temperature. The final microstructure is coarse pearlite.

Normalizing--Heat to at least 55°C above the A_3 line Figure 11.10 (if the concentration of carbon is less than the eutectoid) or above the A_{cm} line (if the concentration of carbon is greater than the eutectoid) until the alloy completely transforms to austenite, then cool in air. The final microstructure is fine pearlite.

Quenching--Heat to a temperature within the austenite phase region and allow the specimen to fully austenitize, then quench to room temperature in oil or water. The final microstructure is martensite.

Tempering--Heat a quenched (martensitic) specimen, to a temperature between 450 and 650°C, for the time necessary to achieve the desired hardness. The final microstructure is tempered martensite.

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11.20 *Cite three sources of internal residual stresses in metal components. What are two possible adverse consequences of these stresses?*

Solution

Three sources of residual stresses in metal components are plastic deformation processes, nonuniform cooling of a piece that was cooled from an elevated temperature, and a phase transformation in which parent and product phases have different densities.

Two adverse consequences of these stresses are distortion (or warpage) and fracture.

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11.21 *Give the approximate minimum temperature at which it is possible to austenitize each of the following iron–carbon alloys during a normalizing heat treatment: (a) 0.20 wt% C, (b) 0.76 wt% C, and (c) 0.95 wt% C.*

Solution

(a) For 0.20 wt% C, heat to at least 905°C (1660°F) since the A_3 temperature is 850°C (1560°F).

(b) For 0.76 wt% C, heat to at least 782°C (1440°F) since the A_3 temperature is 727°C (1340°F).

(c) For 0.95 wt% C, heat to at least 840°C (1545°F) since the A_{cm} temperature is 785°C (1445°F).

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11.22 Give the approximate temperature at which it is desirable to heat each of the following iron–carbon alloys during a full anneal heat treatment: (a) 0.25 wt% C, (b) 0.45 wt% C, (c) 0.85 wt% C, and (d) 1.10 wt% C.

Solution

(a) For 0.25 wt% C, heat to about 880°C (1510°F) since the A_3 temperature is 830°C (1420°F).

(b) For 0.45 wt% C, heat to about 830°C (1525°F) since the A_3 temperature is 780°C (1435°F).

(c) For 0.85 wt% C, heat to about 777°C (1430°F) since the A_1 temperature is 727°C (1340°F).

(d) For 1.10 wt% C, heat to about 777°C (1430°F) since the A_1 temperature is 727°C (1340°F).

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11.23 *What is the purpose of a spheroidizing heat treatment? On what classes of alloys is it normally used?*

Solution

The purpose of a spheroidizing heat treatment is to produce a very soft and ductile steel alloy having a spheroiditic microstructure. It is normally used on medium- and high-carbon steels, which, by virtue of carbon content, are relatively hard and strong.

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Heat Treatment of Steels

11.24 *Briefly explain the difference between hardness and hardenability.*

Solution

Hardness is a measure of a material's resistance to localized surface deformation, whereas hardenability is a measure of the depth to which a ferrous alloy may be hardened by the formation of martensite. Hardenability is determined from hardness tests.

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11.25 *What influence does the presence of alloying elements (other than carbon) have on the shape of a hardenability curve? Briefly explain this effect.*

Solution

The presence of alloying elements (other than carbon) causes a much more gradual decrease in hardness with position from the quenched end for a hardenability curve. The reason for this effect is that alloying elements retard the formation of pearlitic and bainitic structures which are not as hard as martensite.

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11.26 *How would you expect a decrease in the austenite grain size to affect the hardenability of a steel alloy? Why?*

Solution

A decrease of austenite grain size will decrease the hardenability. Pearlite normally nucleates at grain boundaries, and the smaller the grain size, the greater the grain boundary area, and, consequently, the easier it is for pearlite to form.

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11.27 *Name two thermal properties of a liquid medium that will influence its quenching effectiveness.*

Solution

The two thermal properties of a liquid medium that influence its quenching effectiveness are thermal conductivity and heat capacity.

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11.28 *Construct radial hardness profiles for the following:*

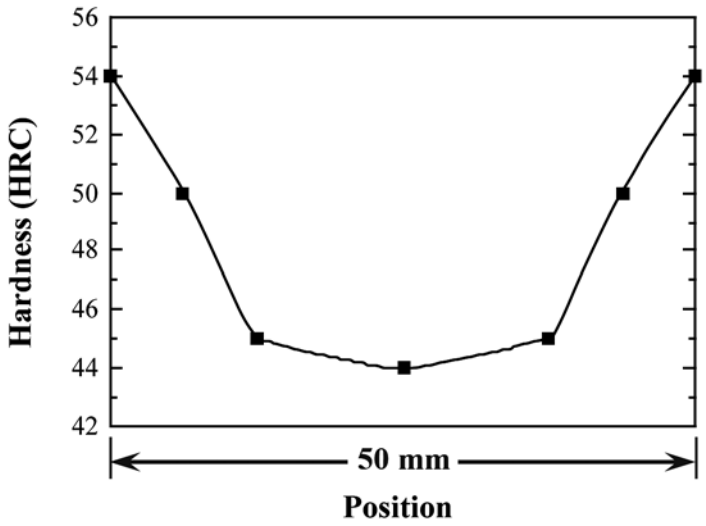
(a) A 50-mm (2-in.) diameter cylindrical specimen of an 8640 steel alloy that has been quenched in moderately agitated oil

Solution

In the manner of Example Problem 11.1, the equivalent distances and hardnesses tabulated below were determined from Figures 11.14 and 11.17*b*.

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	7	54
3/4 *R*	11	50
Midradius	14	45
Center	16	44

The resulting hardness profile is plotted below.



(b) A 75-mm (3-in.) diameter cylindrical specimen of a 5140 steel alloy that has been quenched in moderately agitated oil

Solution

In the manner of Example Problem 11.1, the equivalent distances and hardnesses tabulated below were determined from Figures 11.14 and 11.17*b*.

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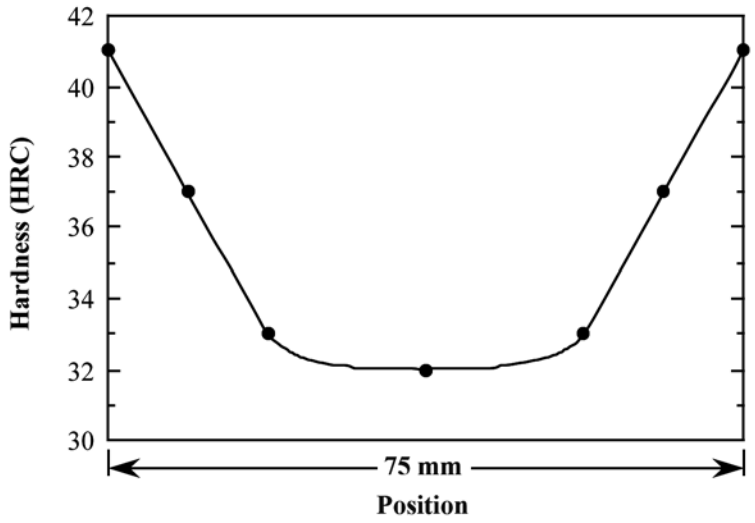
Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	13	41
3/4 *R*	17.5	37
Midradius	22	33
Center	25	32

The resulting hardness profile is plotted below.



(c) A 65-mm ($2\frac{1}{2}$-in.) diameter cylindrical specimen of an 8620 steel alloy that has been quenched in moderately agitated water

Solution

In the manner of Example Problem 11.1, the equivalent distances and hardnesses tabulated below were determined from Figures 11.15 and 11.17*a*.

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	2.5	42
3/4 *R*	7	31
Midradius	11	25
Center	13	24

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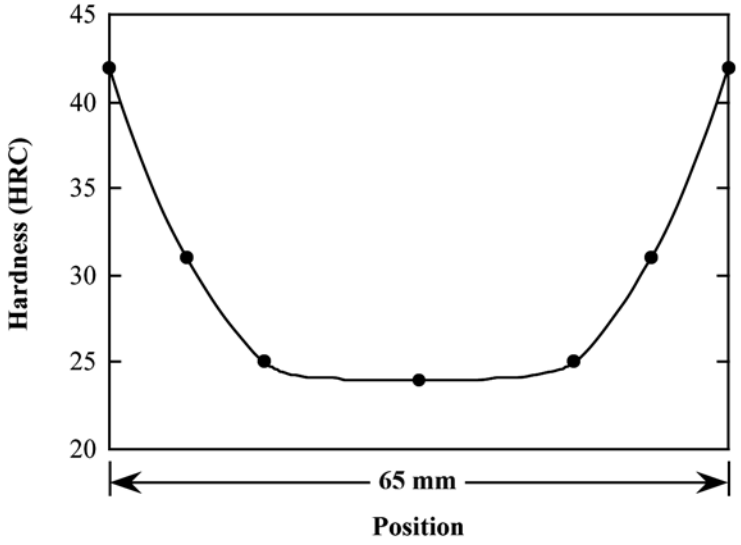
The resulting hardness profile is plotted below.



(d) A 70-mm ($2\frac{3}{4}$-in.) diameter cylindrical specimen of a 1040 steel alloy that has been quenched in moderately agitated water.

Solution

In the manner of Example Problem 11.1, the equivalent distances and hardnesses tabulated below were determined from Figures 11.14 and 11.17*a*.

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	3	48
3/4 *R*	8	30
Midradius	13	23
Center	15	22

The resulting hardness profile is plotted below.

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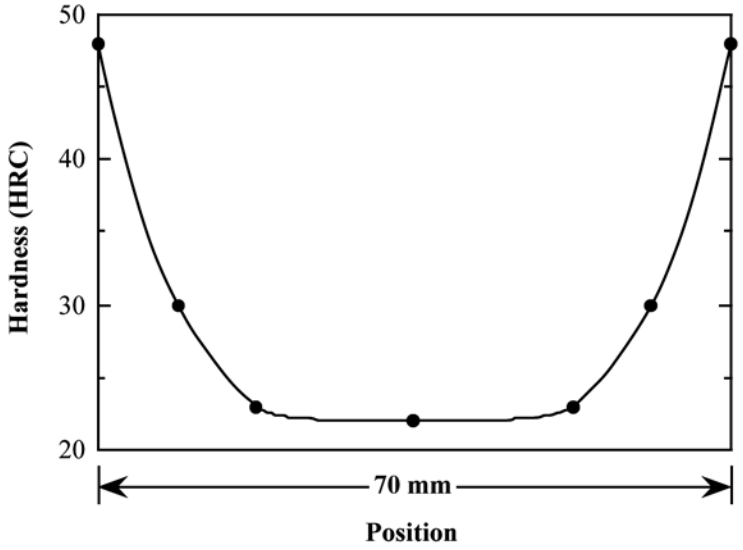

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11.29 *Compare the effectiveness of quenching in moderately agitated water and oil by graphing, on a single plot, radial hardness profiles for 65-mm ($2\frac{1}{2}$-in.) diameter cylindrical specimens of an 8630 steel that have been quenched in both media.*

Solution

We are asked to compare the effectiveness of quenching in moderately agitated water and oil by graphing, on a single plot, hardness profiles for a 65 mm (2-1/2 in.) diameter cylindrical specimen of an 8630 steel that has been quenched in both media.

For moderately agitated water, the equivalent distances and hardnesses for the several radial positions [Figures 11.17*a* and 11.15] are tabulated below.

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	2.5	52
3/4 *R*	7	43
Midradius	11	36
Center	13	33

While for moderately agitated oil, the equivalent distances and hardnesses for the several radial positions [Figures 11.17*b* and 11.15] are tabulated below.

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	10	37
3/4 *R*	15	32
Midradius	18	29
Center	20	28

These data are plotted here.

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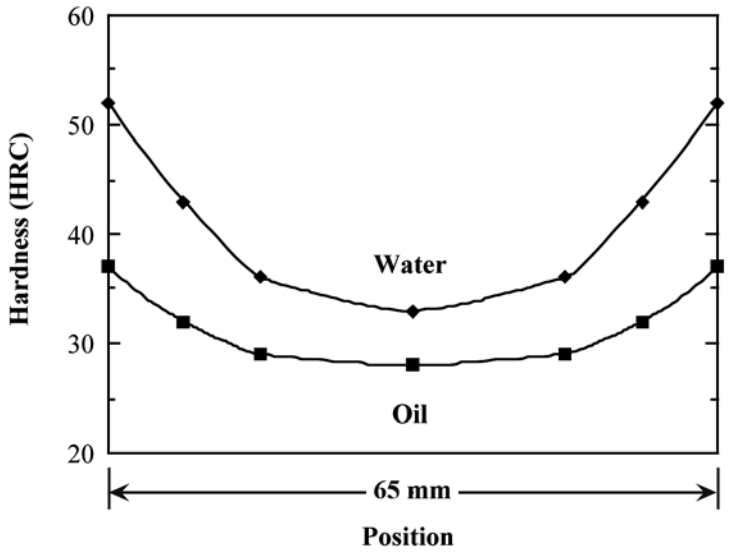

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Precipitation Hardening

11.30 *Compare precipitation hardening (Section 11.9) and the hardening of steel by quenching and tempering (Sections 10.5, 10.6, and 10.8) with regard to*

(a) The total heat treatment procedure

(b) The microstructures that develop

(c) How the mechanical properties change during the several heat treatment stages

Solution

(a) With regard to the total heat treatment procedure, the steps for the *hardening of steel* are as follows:

(1) Austenitize above the upper critical temperature.

(2) Quench to a relatively low temperature.

(3) Temper at a temperature below the eutectoid.

(4) Cool to room temperature.

With regard to *precipitation hardening*, the steps are as follows:

(1) Solution heat treat by heating into the solid solution phase region.

(2) Quench to a relatively low temperature.

(3) Precipitation harden by heating to a temperature that is within the solid two-phase region.

(4) Cool to room temperature.

(b) For the *hardening of steel*, the microstructures that form at the various heat treating stages in part (a) are:

(1) Austenite

(2) Martensite

(3) Tempered martensite

(4) Tempered martensite

For *precipitation hardening*, the microstructures that form at the various heat treating stages in part (a) are:

(1) Single phase

(2) Single phase--supersaturated

(3) Small plate-like particles of a new phase within a matrix of the original phase.

(4) Same as (3)

(c) For the *hardening of steel*, the mechanical characteristics for the various steps in part (a) are as follows:

(1) Not important

(2) The steel becomes hard and brittle upon quenching.

(3) During tempering, the alloy softens slightly and becomes more ductile.

(4) No significant changes upon cooling to or maintaining at room temperature.

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For *precipitation hardening*, the mechanical characteristics for the various steps in part (a) are as follows:

(1) Not important

(2) The alloy is relatively soft.

(3) The alloy hardens with increasing time (initially), and becomes more brittle; it may soften with overaging.

(4) The alloy may continue to harden or overage at room temperature.

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11.31 *What is the principal difference between natural and artificial aging processes?*

Solution

For precipitation hardening, natural aging is allowing the precipitation process to occur at the ambient temperature; artificial aging is carried out at an elevated temperature.

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DESIGN PROBLEMS

Ferrous Alloys
Nonferrous Alloys

11.D1 *Below is a list of metals and alloys:*

Plain carbon steel	*Magnesium*
Brass	*Zinc*
Gray cast iron	*Tool steel*
Platinum	*Aluminum*
Stainless steel	*Tungsten*
Titanium alloy	

Select from this list the one metal or alloy that is best suited for each of the following applications, and cite at least one reason for your choice:

(a) The block of an internal combustion engine

(b) Condensing heat exchanger for steam

(c) Jet engine turbofan blades

(d) Drill bit

(e) Cryogenic (i.e., very low temperature) container

(f) As a pyrotechnic (i.e., in flares and fireworks)

(g) High-temperature furnace elements to be used in oxidizing atmospheres

Solution

(a) Gray cast iron would be the best choice for an engine block because it is relatively easy to cast, is wear resistant, has good vibration damping characteristics, and is relatively inexpensive.

(b) Stainless steel would be the best choice for a heat exchanger to condense steam because it is corrosion resistant to the steam and condensate.

(c) Titanium alloys are the best choice for high-speed aircraft jet engine turbofan blades because they are light weight, strong, and easily fabricated very resistant to corrosion. However, one drawback is their cost.

(d) A tool steel would be the best choice for a drill bit because it is very hard retains its hardness at high temperature and is wear resistant, and, thus, will retain a sharp cutting edge.

(e) For a cryogenic (low-temperature) container, an aluminum alloy would be the best choice; aluminum alloys have an FCC crystal structure, and therefore, are ductile at very low temperatures.

(f) As a pyrotechnic in flares and fireworks, magnesium is the best choice because it ignites easily and burns

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readily in air with a very bright flame.

(g) Platinum is the best choice for high-temperature furnace elements to be used in oxidizing atmospheres because it is very ductile, has a relatively very high melting temperature, and is highly resistant to oxidation.

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11.D2 *A group of new materials are the metallic glasses (or amorphous metals). Write an essay about these materials in which you address the following issues: (1) compositions of some of the common metallic glasses, (2) characteristics of these materials that make them technologically attractive, (3) characteristics that limit their utilization, (4) current and potential uses, and (5) at least one technique that is used to produce metallic glasses.*

Solution

(a) Compositionally, the metallic glass materials are rather complex; several compositions are as follows: $Fe_{80}B_{20}$, $Fe_{72}Cr_8P_{13}C_7$, $Fe_{67}Co_{18}B_{14}Si$, $Pd_{77.5}Cu_{6.0}Si_{16.5}$, and $Fe_{40}Ni_{38}Mo_4B_{18}$.

(b) These materials are exceptionally strong and tough, extremely corrosion resistant, and are easily magnetized.

(c) Principal drawbacks for these materials are 1) complicated and exotic fabrication techniques are required; and 2) inasmuch as very rapid cooling rates are required, at least one dimension of the material must be small--i.e., they are normally produced in ribbon form.

(d) Potential uses include transformer cores, magnetic amplifiers, heads for magnetic tape players, reinforcements for pressure vessels and tires, shields for electromagnetic interference, security tapes for library books.

(e) Production techniques include centrifuge melt spinning, planar-flow casting, rapid pressure application, arc melt spinning.

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11.D3 *Of the following alloys, pick the one(s) that may be strengthened by heat treatment, cold work, or both: R50500 titanium, AZ31B magnesium, 6061 aluminum, C51000 phosphor bronze, lead, 6150 steel, 304 stainless steel, and C17200 beryllium copper.*

Solution

This question provides us with a list of several metal alloys, and then asks us to pick those that may be strengthened by heat treatment, by cold work, or both. Those alloys that may be heat treated are either those noted as "heat treatable" (Tables 11.6 through 11.9), or as martensitic stainless steels (Table 11.4). Alloys that may be strengthened by cold working must not be exceptionally brittle, and, furthermore, must have recrystallization temperatures above room temperature (which immediately eliminates lead). The alloys that fall within the three classifications are as follows:

Heat Treatable	Cold Workable	Both
6150 steel	6150 steel	6150 steel
C17200 Be-Cu	C17200 Be-Cu	C17200 Be-Cu
6061 Al	6061 Al	6061 Al
	304 stainless steel	
	R50500 Ti	
	C51000 phosphor bronze	
	AZ31B Mg	

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11.D4 *A structural member 100 mm (4 in.) long must be able to support a load of 50,000 N (11,250 lb_f) without experiencing any plastic deformation. Given the following data for brass, steel, aluminum, and titanium, rank them from least to greatest weight in accordance with these criteria.*

Alloy	***Yield Strength [MPa (ksi)]***	***Density (g/cm^3)***
Brass	*415 (60)*	*8.5*
Steel	*860 (125)*	*7.9*
Aluminum	*310 (45)*	*2.7*
Titanium	*550 (80)*	*4.5*

Solution

This problem asks us to rank four alloys (brass, steel, titanium, and aluminum), from least to greatest weight for a structural member to support a 50,000 N (11,250 lb_f) load without experiencing plastic deformation. From Equation 6.1, the cross-sectional area (A_0) must necessarily carry the load (F) without exceeding the yield strength (σ_y), as

$$A_0 = \frac{F}{\sigma_y}$$

Now, given the length l, the volume of material required (V) is just

$$V = lA_0 = \frac{lF}{\sigma_y}$$

Finally, the mass of the member (m) is

$$m = V\rho = \frac{\rho lF}{\sigma_y}$$

Here ρ is the density. Using the values given for these alloys

$$m(\text{brass}) = \frac{(8.5\ \text{g/cm}^3)(10\ \text{cm})(50{,}000\ \text{N})}{(415 \times 10^6\ \text{N/m}^2)\left(\frac{1\ \text{m}}{10^2\ \text{cm}}\right)^2} = 102\ \text{g}$$

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$$m(\text{steel}) = \frac{(7.9\ \text{g/cm}^3)(10\ \text{cm})(50{,}000\ \text{N})}{(860 \times 10^6\ \text{N/m}^2)\left(\frac{1\ \text{m}}{10^2\ \text{cm}}\right)^2} = 46\ \text{g}$$

$$m(\text{aluminum}) = \frac{(2.7\ \text{g/cm}^3)(10\ \text{cm})(50{,}000\ \text{N})}{(310 \times 10^6\ \text{N/m}^2)\left(\frac{1\ \text{m}}{10^2\ \text{cm}}\right)^2} = 43.5\ \text{g}$$

$$m(\text{titanium}) = \frac{(4.5\ \text{g/cm}^3)(10\ \text{cm})(50{,}000\ \text{N})}{(550 \times 10^6\ \text{N/m}^2)\left(\frac{1\ \text{m}}{10^2\ \text{cm}}\right)^2} = 40.9\ \text{g}$$

Thus, titanium would have the minimum weight (or mass), followed by aluminum, steel, and brass.

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11.D5 *Discuss whether it would be advisable to hot work or cold work the following metals and alloys on the basis of melting temperature, oxidation resistance, yield strength, and degree of brittleness: tin, tungsten, aluminum alloys, magnesium alloys, and a 4140 steel.*

Solution

Tin would almost always be hot-worked. Even deformation at room temperature would be considered hot-working inasmuch as its recrystallization temperature is below room temperature (Table 7.2).

Tungsten is hard and strong at room temperature, has a high recrystallization temperature, and experiences oxidation at elevated temperatures. Cold-working is difficult because of its strength, and hot-working is not practical because of oxidation problems. Most tungsten articles are fabricated by powder metallurgy, or by using cold-working followed by annealing cycles.

Most aluminum alloys may be cold-worked since they are ductile and have relatively low yield strengths.

Magnesium alloys are normally hot-worked inasmuch as they are quite brittle at room temperature. Also, magnesium alloys have relatively low recrystallization temperatures.

A 4140 steel could be cold-worked in an over-tempered state which leaves it soft and relatively ductile, after which quenching and tempering heat treatments may be employed to strengthen and harden it. This steel would probably have a relatively high recrystallization temperature, and hot-working may cause oxidation.

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Heat Treatment of Steels

11.D6 *A cylindrical piece of steel 25 mm (1.0 in.) in diameter is to be quenched in moderately agitated oil. Surface and center hardnesses must be at least 55 and 50 HRC, respectively. Which of the following alloys will satisfy these requirements: 1040, 5140, 4340, 4140, and 8640? Justify your choice(s).*

Solution

In moderately agitated oil, the equivalent distances from the quenched end for a one-inch diameter bar for surface and center positions are 3 mm (1/8 in.) and 8 mm (11/32 in.), respectively [Figure 11.17*b*]. The hardnesses at these two positions for the alloys cited (as determined using Figure 11.14) are given below.

Alloy	Surface Hardness (HRC)	Center Hardness (HRC)
1040	50	30
5140	56	49
4340	57	57
4140	57	55
8640	57	53

Thus, alloys 4340, 4140, and 8640 will satisfy the criteria for both surface and center hardnesses.

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11.D7 *A cylindrical piece of steel 75 mm (3 in.) in diameter is to be austenitized and quenched such that a minimum hardness of 40 HRC is to be produced throughout the entire piece. Of the alloys 8660, 8640, 8630, and 8620, which will qualify if the quenching medium is (a) moderately agitated water, and (b) moderately agitated oil? Justify your choice(s).*

Solution

(a) This problem calls for us to decide which of 8660, 8640, 8630, and 8620 alloys may be fabricated into a cylindrical piece 75 mm (3 in.) in diameter which, when quenched in mildly agitated water, will produce a minimum hardness of 40 HRC throughout the entire piece.

The center of the steel cylinder will cool the slowest and therefore will be the softest. In moderately agitated water the equivalent distance from the quenched end for a 75 mm diameter bar for the center position is about 17 mm (11/16 in.) [Figure 11.17*a*]. The hardnesses at this position for the alloys cited (Figure 11.15) are given below.

Alloy	Center Hardness (HRC)
8660	58
8640	42
8630	30
8620	22

Therefore, only 8660 and 8640 alloys will have a minimum of 40 HRC at the center, and therefore, throughout the entire cylinder.

(b) This part of the problem asks us to do the same thing for moderately agitated oil. In moderately agitated oil the equivalent distance from the quenched end for a 75 mm diameter bar at the center position is about 25.5 mm (1-1/32 in.) [Figure 11.17*b*]. The hardnesses at this position for the alloys cited (Figure 11.15) are given below.

Alloy	Center Hardness (HRC)
8660	53
8640	37
8630	26
8620	< 20

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Therefore, only the 8660 alloy will have a minimum of 40 HRC at the center, and therefore, throughout the entire cylinder.

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11.D8 *A cylindrical piece of steel 38 mm ($1\frac{1}{2}$ in.) in diameter is to be austenitized and quenched such that a microstructure consisting of at least 80% martensite will be produced throughout the entire piece. Of the alloys 4340, 4140, 8640, 5140, and 1040, which will qualify if the quenching medium is (a) moderately agitated oil and (b) moderately agitated water? Justify your choice(s).*

Solution

(a) Since the cooling rate is lowest at the center, we want a minimum of 80% martensite at the center position. From Figure 11.17*b*, the cooling rate is equal to an equivalent distance from the quenched end of 12 mm (1/2 in.). According to Figure 11.14, the hardness corresponding to 80% martensite for these alloys is 50 HRC. Thus, all we need do is to determine which of the alloys have a 50 HRC hardness at an equivalent distance from the quenched end of 12 mm (1/2 in.). At an equivalent distance of 12 mm (1/2 in.), the following hardnesses are determined from Figure 11.14 for the various alloys.

Alloy	Hardness (HRC)
4340	56
4140	53
8640	49
5140	43
1040	25

Thus, only alloys 4340 and 4140 will qualify.

(b) For moderately agitated water, the cooling rate at the center of a 38 mm diameter specimen is 7 mm (5/16 in.) equivalent distance from the quenched end [Figure 11.17*a*]. At this position, the following hardnesses are determined from Figure 11.14 for the several alloys.

Alloy	Hardness (HRC)
4340	57
4140	55
8640	54
5140	51
1040	33

It is still necessary to have a hardness of 50 HRC or greater at the center; thus, alloys 4340, 4140, 8640, and 5140 qualify.

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11.D9 *A cylindrical piece of steel 90 mm ($3\frac{1}{2}$ in.) in diameter is to be quenched in moderately agitated water. Surface and center hardnesses must be at least 55 and 40 HRC, respectively. Which of the following alloys will satisfy these requirements: 1040, 5140, 4340, 4140, 8620, 8630, 8640, and 8660? Justify your choices.*

Solution

A ninety-millimeter (three and one-half inch) diameter cylindrical steel specimen is to be quenched in moderately agitated water. We are to decide which of eight different steels will have surface and center hardnesses of at least 55 and 40 HRC, respectively.

In moderately agitated water, the equivalent distances from the quenched end for a 90 mm diameter bar for surface and center positions are 3 mm (1/8 in.) and 22 mm (7/8 in.), respectively [Figure 11.17*a*]. The hardnesses at these two positions for the alloys cited are given below. The hardnesses at these two positions for the alloys cited are given below (as determined from Figures 11.14 and 11.15).

Alloy	Surface Hardness (HRC)	Center Hardness (HRC)
1040	50	< 20
5140	56	34
4340	57	53
4140	57	45
8620	42	< 20
8630	51	28
8640	56	38
8660	64	55

Thus, alloys 4340, 4140, and 8660 will satisfy the criteria for both surface hardness (minimum 55 HRC) and center hardness (minimum 40 HRC).

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11.D10 *A cylindrical piece of 4140 steel is to be austenitized and quenched in moderately agitated oil. If the microstructure is to consist of at least 50% martensite throughout the entire piece, what is the maximum allowable diameter? Justify your answer.*

Solution

From Figure 11.14, the equivalent distance from the quenched end of a 4140 steel to give 50% martensite (or a 42.5 HRC hardness) is 27 mm (1-1/8 in.). Thus, the quenching rate at the center of the specimen should correspond to this equivalent distance. Using Figure 11.17*b*, the center specimen curve takes on a value of 27 mm (1-1/8 in.) equivalent distance at a diameter of about 83 mm (3.3 in.).

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11.D11 *A cylindrical piece of 8640 steel is to be austenitized and quenched in moderately agitated oil. If the hardness at the surface of the piece must be at least 49 HRC, what is the maximum allowable diameter? Justify your answer.*

Solution

We are to determine, for a cylindrical piece of 8640 steel, the minimum allowable diameter possible in order yield a surface hardness of 49 HRC, when the quenching is carried out in moderately agitated oil.

From Figure 11.15, the equivalent distance from the quenched end of an 8640 steel to give a hardness of 49 HRC is about 12 mm (15/32 in.). Thus, the quenching rate at the surface of the specimen should correspond to this equivalent distance. Using Figure 11.17*b*, the surface specimen curve takes on a value of 12 mm equivalent distance at a diameter of about 75 mm (3 in.).

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11.D12 *Is it possible to temper an oil-quenched 4140 steel cylindrical shaft 100 mm (4 in.) in diameter so as to give a minimum tensile strength of 850 MPa (125,000 psi) and a minimum ductility of 21%EL? If so, specify a tempering temperature. If this is not possible, then explain why.*

Solution

This problem asks if it is possible to temper an oil-quenched 4140 steel cylindrical shaft 100 mm (4 in.) in diameter so as to give a minimum tensile strength of 850 MPa (125,000 psi) and a minimum ductility of 21%EL. In order to solve this problem it is necessary to use Figures 11.20*a* and 11.20*c*, which plot, respectively, tensile strength and ductility versus tempering temperature. For the 100 mm diameter line of Figure 11.20*a*, tempering temperatures less than about 560°C are required to give a tensile strength of at least 850 MPa. Furthermore, from Figure 11.20*c*, for the 100 mm diameter line, tempering temperatures greater than about 585°C will give ductilities greater than 21%EL. Hence, it *is not possible* to temper this alloy to produce the stipulated minimum tensile strength and ductility. To meet the tensile strength minimum, T(tempering) < 560°C, whereas for ductility minimum, T(tempering) > 585°C; thus, there is no overlap of these tempering temperature ranges.

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11.D13 *Is it possible to temper an oil-quenched 4140 steel cylindrical shaft 12.5 mm (0.5 in.) in diameter so as to give a minimum yield strength of 1000 MPa (145,000 psi) and a minimum ductility of 16%EL? If so, specify a tempering temperature. If this is not possible, then explain why.*

Solution

This problem asks if it is possible to temper an oil-quenched 4140 steel cylindrical shaft 12.5 mm (0.5 in.) in diameter so as to give a minimum yield strength of 1000 MPa (145,000 psi) and a minimum ductility of 16%EL. In order to solve this problem it is necessary to use Figures 11.20*b* and 11.20*c*, which plot, respectively, yield strength and ductility versus tempering temperature. For the 12.5 mm diameter line of Figure 11.20*b*, tempering temperatures less than about 600°C are required to give a yield strength of at least 1000 MPa. Furthermore, from Figure 11.20*c*, for the 12.5 mm diameter line, tempering temperatures greater than about 550°C will give ductilities greater than 17%EL. Hence, it *is possible* to temper this alloy to produce the stipulated minimum yield strength and ductility; the tempering temperature will lie between 550°C and 600°C.

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Precipitation Hardening

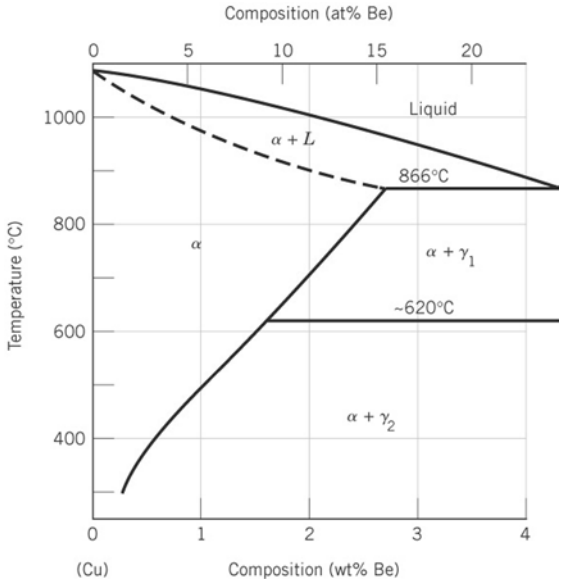
11.D14 *Copper-rich copper–beryllium alloys are precipitation hardenable. After consulting the portion of the phase diagram (Figure 11.30), do the following:*

(a) Specify the range of compositions over which these alloys may be precipitation hardened.

(b) Briefly describe the heat-treatment procedures (in terms of temperatures) that would be used to precipitation harden an alloy having a composition of your choosing, yet lying within the range given for part (a).

Solution

This problem is concerned with the precipitation-hardening of copper-rich Cu-Be alloys. It is necessary for us to use the Cu-Be phase diagram (Figure 11.30), which is shown below.



(a) The range of compositions over which these alloys may be precipitation hardened is between approximately 0.2 wt% Be (the maximum solubility of Be in Cu at about 300°C) and 2.7 wt% Be (the maximum solubility of Be in Cu at 866°C).

(b) The heat treatment procedure, of course, will depend on the composition chosen. First of all, the solution heat treatment must be carried out at a temperature within the α phase region, after which, the specimen is quenched to room temperature. Finally, the precipitation heat treatment is conducted at a temperature within the $\alpha + \gamma_2$ phase region.

For example, for a 1.5 wt% Be-98.5 wt% Cu alloy, the solution heat treating temperature must be between about 600°C (1110°F) and 900°C (1650°F), while the precipitation heat treatment would be below 600°C (1110°F),

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and probably above 300°C (570°F). Below 300°C, diffusion rates are low, and heat treatment times would be relatively long.

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11.D15 *A solution heat-treated 2014 aluminum alloy is to be precipitation hardened to have a minimum tensile strength of 450 MPa (65,250 psi) and a ductility of at least 15%EL. Specify a practical precipitation heat treatment in terms of temperature and time that would give these mechanical characteristics. Justify your answer.*

Solution

We are asked to specify a practical heat treatment for a 2014 aluminum alloy that will produce a minimum tensile strength of 450 MPa (65,250 psi), and a minimum ductility of 15%EL. From Figure 11.27*a*, the following heat treating temperatures and time ranges are possible to the give the required tensile strength.

Temperature (°C)	Time Range (h)
260	0.02-0.2
204	0.02-10
149	3-600
121	> 35-?

With regard to temperatures and times to give the desired ductility [Figure 11.27*b*]:

Temperature (°C)	Time Range (h)
260	< 0.01, > 40
204	< 0.15
149	< 10
121	< 500

From these tabulations, the following may be concluded:

It is not possible to heat treat this alloy at 260°C so as to produce the desired set of properties— there is no overlap of the two sets of time ranges.

At 204°C, the heat treating time would be between 0.02 and 0.15 h; times lying within this range are impractically short.

At 149°C, the time would be between 3 and 10 h.

Finally, at 121°C, the time range is 35 to about 500 h.

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11.D16 *Is it possible to produce a precipitation-hardened 2014 aluminum alloy having a minimum tensile strength of 425 MPa (61,625 psi) and a ductility of at least 12%EL? If so, specify the precipitation heat treatment. If it is not possible, explain why.*

Solution

This problem inquires as to the possibility of producing a precipitation-hardened 2014 aluminum alloy having a minimum tensile strength of 425 MPa (61,625 psi) and a ductility of at least 12%EL. In order to solve this problem it is necessary to consult Figures 11.27*a* and 11.27*b*. Below are tabulated the times required at the various temperatures to achieve the stipulated tensile strength.

Temperature (°C)	Time Range (h)
260	< 0.5
204	< 15
149	1-1000
121	> 35-?

With regard to temperatures and times to give the desired ductility:

Temperature (°C)	Time Range (h)
260	< 0.02, > 10
204	< 0.4, > 350
149	< 20
121	< 1000

From these tabulations, the following may be concluded:

At 260°C, the heat treating time would need to be less than 0.02 h (1.2 min), which is impractically short.

At 204°C, the heat treatment would need to be less than 0.4 h (24 min), which is a little on the short side.

At 149°C, the time range would be between 1 and 20 h.

Finally, at 121°C, this property combination is possible for virtually all times less than about 1000 h.

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CHAPTER 12

STRUCTURES AND PROPERTIES OF CERAMICS

PROBLEM SOLUTIONS

Crystal Structures

12.1 *For a ceramic compound, what are the two characteristics of the component ions that determine the crystal structure?*

Solution

The two characteristics of component ions that determine the crystal structure of a ceramic compound are: 1) the magnitude of the electrical charge on each ion, and 2) the relative sizes of the cations and anions.

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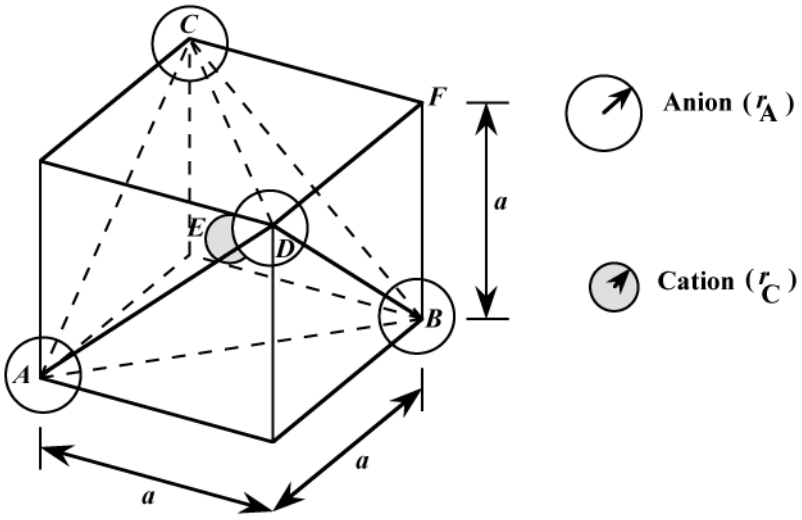
12.2 *Show that the minimum cation-to-anion radius ratio for a coordination number of 4 is 0.225.*

Solution

In this problem we are asked to show that the minimum cation-to-anion radius ratio for a coordination number of four is 0.225. If lines are drawn from the centers of the anions, then a tetrahedron is formed. The tetrahedron may be inscribed within a cube as shown below.



The spheres at the apexes of the tetrahedron are drawn at the corners of the cube, and designated as positions *A*, *B*, *C*, and *D*. (These are reduced in size for the sake of clarity.) The cation resides at the center of the cube, which is designated as point *E*. Let us now express the cation and anion radii in terms of the cube edge length, designated as *a*. The spheres located at positions *A* and *B* touch each other along the bottom face diagonal. Thus,

$$\overline{AB} = 2r_A$$

But

$$(\overline{AB})^2 = a^2 + a^2 = 2a^2$$

or

$$\overline{AB} = a\sqrt{2} = 2r_A$$

And

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$$a = \frac{2r_A}{\sqrt{2}}$$

There will also be an anion located at the corner, point *F* (not drawn), and the cube diagonal $\overline{AEF}$ will be related to the ionic radii as

$$\overline{AEF} = 2(r_A + r_C)$$

(The line *AEF* has not been drawn to avoid confusion.) From the triangle *ABF*

$$(\overline{AB})^2 + (\overline{FB})^2 = (\overline{AEF})^2$$

But,

$$\overline{FB} = a = \frac{2r_A}{\sqrt{2}}$$

and

$$\overline{AB} = 2r_A$$

from above. Thus,

$$(2r_A)^2 + \left(\frac{2r_A}{\sqrt{2}}\right)^2 = [2(r_A + r_C)]^2$$

Solving for the r_C/r_A ratio leads to

$$\frac{r_C}{r_A} = \frac{\sqrt{6} - 2}{2} = 0.225$$

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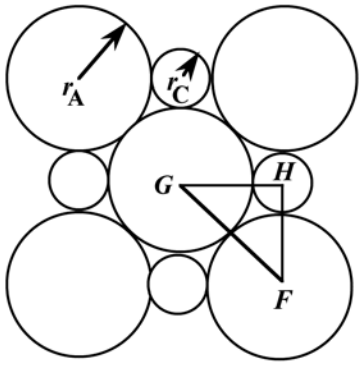
12.3 *Show that the minimum cation-to-anion radius ratio for a coordination number of 6 is 0.414. [Hint: Use the NaCl crystal structure (Figure 12.2), and assume that anions and cations are just touching along cube edges and across face diagonals.]*

Solution

This problem asks us to show that the minimum cation-to-anion radius ratio for a coordination number of 6 is 0.414 (using the rock salt crystal structure). Below is shown one of the faces of the rock salt crystal structure in which anions and cations just touch along the edges, and also the face diagonals.



From triangle *FGH*,

$$\overline{GF} = 2r_A$$

and

$$\overline{FH} = \overline{GH} = r_A + r_C$$

Since *FGH* is a right triangle

$$(\overline{GH})^2 + (\overline{FH})^2 = (\overline{FG})^2$$

or

$$(r_A + r_C)^2 + (r_A + r_C)^2 = (2r_A)^2$$

which leads to

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$$r_A + r_C = \frac{2r_A}{\sqrt{2}}$$

Or, solving for r_C/r_A

$$\frac{r_C}{r_A} = \left(\frac{2}{\sqrt{2}} - 1\right) = 0.414$$

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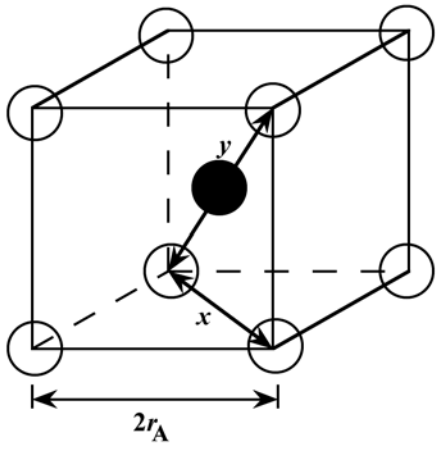
12.4 *Demonstrate that the minimum cation-to-anion radius ratio for a coordination number of 8 is 0.732.*

Solution

This problem asks us to show that the minimum cation-to-anion radius ratio for a coordination number of 8 is 0.732. From the cubic unit cell shown below



the unit cell edge length is $2r_A$, and from the base of the unit cell

$$x^2 = (2r_A)^2 + (2r_A)^2 = 8r_A^2$$

Or

$$x = 2r_A\sqrt{2}$$

Now from the triangle that involves x, y, and the unit cell edge

$$x^2 + (2r_A)^2 = y^2 = (2r_A + 2r_C)^2$$

$$(2r_A\sqrt{2})^2 + 4r_A^2 = (2r_A + 2r_C)^2$$

Which reduces to

$$2r_A(\sqrt{3} - 1) = 2r_C$$

Or

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$$\frac{r_C}{r_A} = \sqrt{3} - 1 = 0.732$$

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12.5 *On the basis of ionic charge and ionic radii given in Table 12.3, predict crystal structures for the following materials:*

(a) CsI,

(b) NiO,

(c) KI, and

(d) NiS.

Justify your selections.

Solution

This problem calls for us to predict crystal structures for several ceramic materials on the basis of ionic charge and ionic radii.

(a) For CsI, using data from Table 12.3

$$\frac{r_{Cs^+}}{r_{I^-}} = \frac{0.170\ \text{nm}}{0.220\ \text{nm}} = 0.773$$

Now, from Table 12.2, the coordination number for each cation (Cs^+) is eight, and, using Table 12.4, the predicted crystal structure is cesium chloride.

(b) For NiO, using data from Table 12.3

$$\frac{r_{Ni^{2+}}}{r_{O^{2-}}} = \frac{0.069\ \text{nm}}{0.140\ \text{nm}} = 0.493$$

The coordination number is six (Table 12.2), and the predicted crystal structure is sodium chloride (Table 12.4).

(c) For KI, using data from Table 12.3

$$\frac{r_{K^+}}{r_{I^-}} = \frac{0.138\ \text{nm}}{0.220\ \text{nm}} = 0.627$$

The coordination number is six (Table 12.2), and the predicted crystal structure is sodium chloride (Table 12.4).

(d) For NiS, using data from Table 12.3

$$\frac{r_{Ni^{2+}}}{r_{S^{2-}}} = \frac{0.069\ \text{nm}}{0.184\ \text{nm}} = 0.375$$

The coordination number is four (Table 12.2), and the predicted crystal structure is zinc blende (Table 12.4).

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12.6 *Which of the cations in Table 12.3 would you predict to form iodides having the cesium chloride crystal structure? Justify your choices.*

Solution

We are asked to cite the cations in Table 12.3 which would form iodides having the cesium chloride crystal structure. First of all, the possibilities would include only the monovalent cations Cs^+, K^+, and Na^+. Furthermore, the coordination number for each cation must be 8, which means that $0.732 < r_C/r_A < 1.0$ (Table 12.2). From Table 12.3 the r_C/r_A ratios for these three cations and the I^- ion are as follows:

$$\frac{r_{Cs^+}}{r_{I^-}} = \frac{0.170 \text{ nm}}{0.220 \text{ nm}} = 0.77$$

$$\frac{r_{K^+}}{r_{I^-}} = \frac{0.138 \text{ nm}}{0.220 \text{ nm}} = 0.63$$

$$\frac{r_{Na^+}}{r_{I^-}} = \frac{0.102 \text{ nm}}{0.220 \text{ nm}} = 0.46$$

Thus, only cesium will form the CsCl crystal structure with iodine.

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12.7 *Compute the atomic packing factor for the rock salt crystal structure in which $r_C/r_A = 0.414$.*

Solution

This problem asks that we compute the atomic packing factor for the rock salt crystal structure when $r_C/r_A = 0.414$. From Equation 3.2

$$\text{APF} = \frac{V_S}{V_C}$$

With regard to the sphere volume, V_S, there are four cation and four anion spheres per unit cell. Thus,

$$V_S = (4)\left(\frac{4}{3}\pi r_A^3\right) + (4)\left(\frac{4}{3}\pi r_C^3\right)$$

But, since $r_C/r_A = 0.414$

$$V_S = \frac{16}{3}\pi r_A^3\left[1 + (0.414)^3\right] = (17.94)\, r_A^3$$

Now, for $r_C/r_A = 0.414$ the corner anions in Table 12.2 just touch one another along the cubic unit cell edges such that

$$V_C = a^3 = \left[2(r_A + r_C)\right]^3$$

$$= \left[2(r_A + 0.414 r_A)\right]^3 = (22.62) r_A^3$$

Thus

$$\text{APF} = \frac{V_S}{V_C} = \frac{(17.94)\, r_A^3}{(22.62)\, r_A^3} = 0.79$$

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12.8 *The zinc blende crystal structure is one that may be generated from close-packed planes of anions.*

(a) Will the stacking sequence for this structure be FCC or HCP? Why?

(b) Will cations fill tetrahedral or octahedral positions? Why?

(c) What fraction of the positions will be occupied?

Solution

This question is concerned with the zinc blende crystal structure in terms of close-packed planes of anions.

(a) The stacking sequence of close-packed planes of anions for the zinc blende crystal structure will be the same as FCC (and not HCP) because the anion packing is FCC (Table 12.4).

(b) The cations will fill tetrahedral positions since the coordination number for cations is four (Table 12.4).

(c) Only one-half of the tetrahedral positions will be occupied because there are two tetrahedral sites per anion, and yet only one cation per anion.

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12.9 *The corundum crystal structure, found for Al_2O_3, consists of an HCP arrangement of O^{2-} ions; the Al^{3+} ions occupy octahedral positions.*

(a) What fraction of the available octahedral positions are filled with Al^{3+} ions?

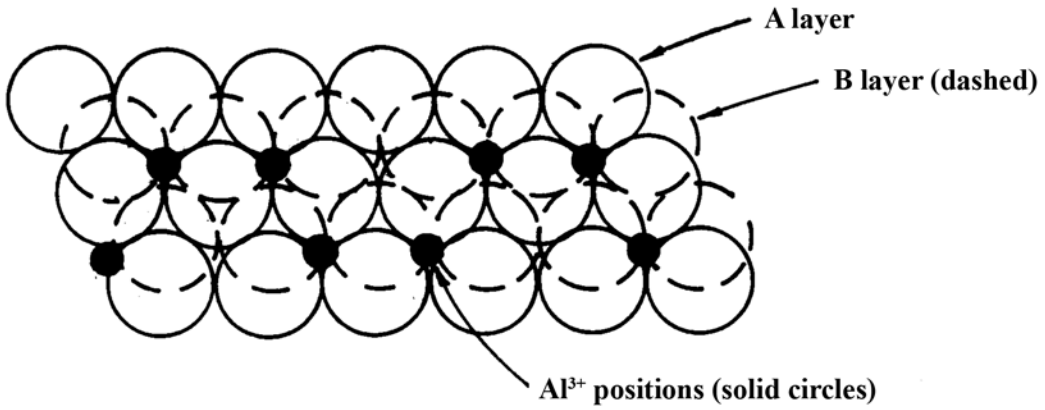
(b) Sketch two close-packed O^{2-} planes stacked in an AB sequence, and note octahedral positions that will be filled with the Al^{3+} ions.

Solution

This question is concerned with the corundum crystal structure in terms of close-packed planes of anions.

(a) For this crystal structure, two-thirds of the octahedral positions will be filled with Al^{3+} ions since there is one octahedral site per O^{2-} ion, and the ratio of Al^{3+} to O^{2-} ions is two-to-three.

(b) Two close-packed O^{2-} planes and the octahedral positions between these planes that will be filled with Al^{3+} ions are sketched below.



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12.10 *Iron sulfide (FeS) may form a crystal structure that consists of an HCP arrangement of S^{2-} ions.*

(a) Which type of interstitial site will the Fe^{2+} ions occupy?

(b) What fraction of these available interstitial sites will be occupied by Fe^{2+} ions?

Solution

(a) This portion of the problem asks that we specify which type of interstitial site the Fe^{2+} ions will occupy in FeS if the S^{2-} ions form an HCP arrangement. Since, from Table 12.3, $r_{S^{2-}} = 0.184$ nm and $r_{Fe^{2+}} = 0.077$ nm, then

$$\frac{r_{Fe^{2+}}}{r_{S^{2-}}} = \frac{0.077 \text{ nm}}{0.184 \text{ nm}} = 0.418$$

Inasmuch as r_C/r_A is between 0.414 and 0.732, the coordination number for Fe^{2+} is 6 (Table 12.2); therefore, tetrahedral octahedral positions are occupied.

(b) We are now asked what fraction of these available interstitial sites are occupied by Fe^{2+} ions. Since there is 1 octahedral site per S^{2-} ion, and the ratio of Fe^{2+} to S^{2-} is 1:1, all of these sites are occupied with Fe^{2+} ions.

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12.11 *Magnesium silicate, Mg_2SiO_4, forms in the olivine crystal structure that consists of an HCP arrangement of O^{2-} ions.*

(a) Which type of interstitial site will the Mg^{2+} ions occupy? Why?

(b) Which type of interstitial site will the Si^{4+} ions occupy? Why?

(c) What fraction of the total tetrahedral sites will be occupied?

(d) What fraction of the total octahedral sites will be occupied?

Solution

(a) We are first of all asked to cite, for Mg_2SiO_4, which type of interstitial site the Mg^{2+} ions will occupy. From Table 12.3, the cation-anion radius ratio is

$$\frac{r_{Mg^{2+}}}{r_{O^{2-}}} = \frac{0.072\ \text{nm}}{0.140\ \text{nm}} = 0.514$$

Since this ratio is between 0.414 and 0.732, the Mg^{2+} ions will occupy octahedral sites (Table 12.2).

(b) Similarly, for the Si^{4+} ions

$$\frac{r_{Si^{4+}}}{r_{O^{2-}}} = \frac{0.040\ \text{nm}}{0.140\ \text{nm}} = 0.286$$

Since this ratio is between 0.225 and 0.414, the Si^{4+} ions will occupy tetrahedral sites.

(c) For each Mg_2SiO_4 formula unit, there are four O^{2-} ions, and, therefore, eight tetrahedral sites; furthermore, since there is one Si^{4+} ion per four O^{2-} ions (eight tetrahedral sites), one-eighth of the tetrahedral sites will be occupied.

(d) Also, inasmuch as the Mg^{2+} to O^{2-} ratio is 1:2, and there is one octahedral site per O^{2-} ion, one-half of these sites will be filled.

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12.12 *Using the Molecule Definition Utility found in both "Metallic Crystal Structures and Crystallography" and "Ceramic Crystal Structures" modules of VMSE, located on the book's web site [www.wiley.com/college/callister (Student Companion Site)], generate (and print out) a three-dimensional unit cell for titanium dioxide, TiO_2, given the following: (1) The unit cell is tetragonal with a = 0.459 nm and c = 0.296 nm, (2) oxygen atoms are located at the following point coordinates:*

0.356 0.356 0 *0.856 0.144* $\frac{1}{2}$

0.664 0.664 0 *0.144 0.856* $\frac{1}{2}$

and (3) Ti atoms are located at the following point coordinates:

0 0 0 *1 0 1*

1 0 0 *0 1 1*

0 1 0 *1 1 1*

0 0 1 $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$

1 1 0

Solution

First of all, open the "Molecular Definition Utility"; it may be found in either of "Metallic Crystal Structures and Crystallography" or "Ceramic Crystal Structures" modules.

In the "Step 1" window, it is necessary to define the atom types, colors for the spheres (atoms), and specify atom sizes. Let us enter "O" as the name for the oxygen ions (since "O" the symbol for oxygen), and "Ti" as the name for the titanium ions. Next it is necessary to choose a color for each atom type from the selections that appear in the pull-down menu—for example, "Red" for O and "Light Cyan" for Ti. In the "Atom Size" window, it is necessary to enter an atom/ion size. In the instructions for this step, it is suggested that the atom/ion diameter in nanometers be used. From the table found inside the front cover of the textbook, the atomic radii for oxygen and titanium are 0.140 nm and 0.068 nm, respectively, and, therefore, their ionic diameters are twice these values (i.e., 0.280 nm and 0.136 nm); therefore, we enter the values "0.280" and "0.136" for the two atom types. Now click on the "Register" button, followed by clicking on the "Go to Step 2" button.

In the "Step 2" window we specify positions for all of the atoms within the unit cell; their point coordinates are specified in the problem statement. Let's begin with oxygen. Click on the red sphere that is located to the right of the "Molecule Definition Utility" box. Some of the point coordinates for the oxygen ions are fractional ones; in these instances, the unit cell lattice parameters--*a* or *c* (i.e., 0.459 or 0.296) are multiplied by the fraction. For example, one oxygen ion is located at the 0.856 0.144 $\frac{1}{2}$coordinate. Therefore, the x, y, and z atoms positions are (0.856)(0.459) = 0.393, (0.144)(0.459) = 0.066, and $\frac{1}{2}$(0.296) = 0.148, respectively. Thus, we enter "0.393" in the "x" position box, "0.066" in the "y" position box, and "0.148" in the "z" position box. [*Note:* the

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first two point coordinates relate to the *a* lattice parameter (0.459 nm), whereas the third applies to the *c* lattice parameter (0.296 nm).] Next we click on the "Register Atom Position" button. Now we repeat the procedure for the remaining oxygen ions

After this step has been completed, it is necessary to specify positions for the titanium ions. To begin, we click on the light cyan sphere that is located next to the "Molecule Definition Utility" box. One Ti ion will be positioned at the origin of the coordinate system—i.e., its point coordinates are 0 0 0, and, therefore, we enter a "0" (zero) in each of the "x", "y", and "z" atom position boxes. Next we click on the "Register Atom Position" button. And the enter the coordinate for all of the other titanium ions

For the oxygen ions, x, y, and z atom position entries for the 4 sets of point coordinates are as follows:

0.163, 0.163, 0

0.305, 0.305, 0

0.393, 0.066, 0.148

0.066, 0.393, 0.148

Now, for the titanium ions, the x, y, and z atom position entries for all 9 sets of point coordinates are as follows:

0, 0, 0

0.459, 0, 0

0, 0.459, 0

0, 0, 0.296

0.459, 0.459, 0

0.459, 0, 0.296

0, 0.459, 0.296

0.459, 0.459, 0.296

0.230, 0.230, 0.148

In Step 3, we may specify which atoms are to be represented as being bonded to one another, and which type of bond(s) to use (single solid, single dashed, double, and triple are possibilities), or we may elect to not represent any bonds at all (in which case we are finished). If it is decided to show bonds, probably the best thing to do is to represent unit cell edges as bonds. Your resulting image may be rotated by using mouse click-and-drag

Your image should appear as the following screen shot.

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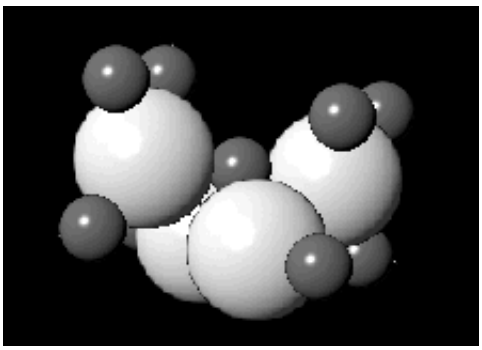

Here the darker spheres represent titanium ions, while oxygen ions are depicted by the lighter balls.

[Note: Unfortunately, with this version of the Molecular Definition Utility, it is not possible to save either the data or the image that you have generated. You may use screen capture (or screen shot) software to record and store your image.]

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12.13 *Calculate the density of FeO, given that it has the rock salt crystal structure.*

Solution

We are asked to calculate the theoretical density of FeO. This density may be computed using Equation (12.1) as

$$\rho = \frac{n'\left(A_{Fe} + A_O\right)}{V_C N_A}$$

Since the crystal structure is rock salt, $n' = 4$ formula units per unit cell. Using the ionic radii for Fe^{2+} and O^{2-} from Table 12.3, the unit cell volume is computed as follows:

$$V_C = a^3 = \left(2r_{Fe^{2+}} + 2r_{O^{2-}}\right)^3 = \left[2\,(0.077\ \text{nm}) + 2\,(0.140\ \text{nm})\right]^3$$

$$= 0.0817\ \frac{\text{nm}^3}{\text{unit cell}} = 8.17 \times 10^{-23}\ \frac{\text{cm}^3}{\text{unit cell}}$$

Thus,

$$\rho = \frac{(4\ \text{formula units/unit cell})(55.85\ \text{g/mol} + 16.00\ \text{g/mol})}{\left(8.17 \times 10^{-23}\ \text{cm}^3\text{/unit cell}\right)\left(6.022 \times 10^{23}\ \text{formula units/mol}\right)}$$

$$= 5.84\ \text{g/cm}^3$$

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12.14 *Magnesium oxide has the rock salt crystal structure and a density of 3.58 g/cm^3.*

(a) Determine the unit cell edge length.

(b) How does this result compare with the edge length as determined from the radii in Table 12.3, assuming that the Mg^{2+} and O^{2-} ions just touch each other along the edges?

Solution

(a) This part of the problem calls for us to determine the unit cell edge length for MgO. The density of MgO is 3.58 g/cm^3 and the crystal structure is rock salt. From Equation 12.1

$$\rho = \frac{n'(A_{Mg} + A_O)}{V_C N_A} = \frac{n'(A_{Mg} + A_O)}{a^3 N_A}$$

Or, solving for a

$$a = \left[\frac{n'(A_{Mg} + A_O)}{\rho N_A}\right]^{1/3}$$

Inasmuch as there are 4 formula units per unit cell for the rock salt crystal structure, and the atomic weights of magnesium and oxygen are 24.31 and 16.00 g/mol, respectively, when we solve for a from the above equation

$$a = \left[\frac{(4 \text{ formula units/unit cell})(24.31 \text{ g/mol} + 16.00 \text{ g/mol})}{(3.58 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ formula units/mol})}\right]^{1/3}$$

$$= 4.21 \times 10^{-8} \text{ cm} = 0.421 \text{ nm}$$

(b) The edge length is determined from the Mg^{2+} and O^{2-} radii for this portion of the problem. Now for the rock salt crystal structure

$$a = 2r_{Mg^{2+}} + 2r_{O^{2-}}$$

From Table 12.3

$$a = 2(0.072 \text{ nm}) + 2(0.140 \text{ nm}) = 0.424 \text{ nm}$$

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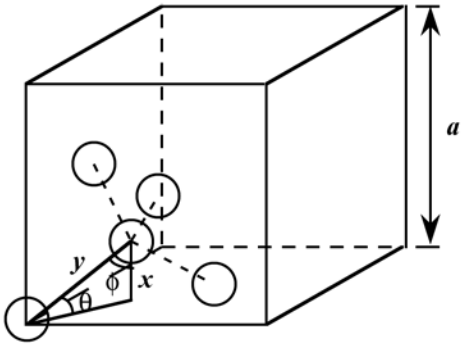
12.15 *Compute the theoretical density of diamond given that the C—C distance and bond angle are 0.154 nm and 109.5°, respectively. How does this value compare with the measured density?*

Solution

This problem asks that we compute the theoretical density of diamond given that the C—C distance and bond angle are 0.154 nm and 109.5°, respectively. The first thing we need do is to determine the unit cell edge length from the given C—C distance. The drawing below shows the cubic unit cell with those carbon atoms that bond to one another in one-quarter of the unit cell.



From this figure, ϕ is one-half of the bond angle or $\phi = 109.5°/2 = 54.75°$, which means that

$$\theta = 90° - 54.75° = 35.25°$$

since the triangle shown is a right triangle. Also, $y = 0.154$ nm, the carbon-carbon bond distance. Furthermore, $x = a/4$, and therefore,

$$x = \frac{a}{4} = y \sin\theta$$

Or

$$a = 4y \sin\theta = (4)(0.154\ \text{nm})(\sin 35.25°) = 0.356\ \text{nm}$$

$$= 3.56 \times 10^{-8}\ \text{cm}$$

The unit cell volume, V_C is just a^3, that is

$$V_C = a^3 = (3.56 \times 10^{-8}\ \text{cm})^3 = 4.51 \times 10^{-23}\ \text{cm}^3$$

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We must now utilize a modified Equation 12.1 since there is only one atom type. There are 8 equivalent atoms per unit cell, and therefore

$$\rho = \frac{n\tilde{O}A_C}{V_C N_A}$$

$$= \frac{(8 \text{ atoms/unit cell})(12.01 \text{ g/g - atom})}{\left(4.51 \times 10^{-23} \text{ cm}^3\text{/unit cell}\right)\left(6.022 \times 10^{23} \text{ atoms/g - atom}\right)}$$

$$= 3.54 \text{ g/cm}^3$$

The measured density is 3.51 g/cm^3.

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12.16 *Compute the theoretical density of ZnS given that the Zn—S distance and bond angle are 0.234 nm and 109.5°, respectively. How does this value compare with the measured density?*

Solution

This problem asks that we compute the theoretical density of ZnS given that the Zn—S distance and bond angle are 0.234 nm and 109.5°, respectively. The first thing we need do is to determine the unit cell volume from the given Zn—S distance. From the previous problem, the unit cell volume V_C is just a^3, a being the unit cell edge length, and

$$V_C = (4y \sin\theta)^3 = [(4)(0.234\text{ nm})(\sin 35.25°)]^3$$

$$= 0.1576\text{ nm}^3 = 1.576 \times 10^{-22}\text{ cm}^3$$

Now we must utilize Equation 12.1 with $n' = 4$ formula units, and A_{Zn} and A_S being 65.41 and 32.06 g/mol, respectively. Thus

$$\rho = \frac{n'(A_{Zn} + A_S)}{V_C N_A}$$

$$= \frac{(4\text{ formula units/unit cell})(65.41\text{ g/mol} + 32.06\text{ g/mol})}{(1.576 \times 10^{-22}\text{ cm}^3\text{/unit cell})(6.022 \times 10^{23}\text{ formula units/mol})}$$

$$= 4.11\text{ g/cm}^3$$

The measured value of the density is 4.10 g/cm^3.

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12.17 *Cadmium sulfide (CdS) has a cubic unit cell, and from x-ray diffraction data it is known that the cell edge length is 0.582 nm. If the measured density is 4.82 g/cm^3, how many Cd^{2+} and S^{2-} ions are there per unit cell?*

Solution

We are asked to determine the number of Cd^{2+} and S^{2-} ions per unit cell for cadmium sulfide (CdS). For CdS, $a = 0.582$ nm and $\rho = 4.82$ g/cm^3. Solving for n' from Equation 12.1, we get

$$n' = \frac{\rho V_C N_A}{A_{Cd} + A_S} = \frac{\rho a^3 N_A}{A_{Cd} + A_S}$$

$$= \frac{(4.82 \text{ g/cm}^3)(5.82 \times 10^{-8} \text{ cm})^3 (6.022 \times 10^{23} \text{ formula units/mol})}{(112.41 \text{ g/mol} + 32.06 \text{ g/mol})}$$

$$= 3.96 \text{ or almost } 4$$

Therefore, there are four Cd^{2+} and four S^{2-} per unit cell.

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12.18 *(a) Using the ionic radii in Table 12.3, compute the theoretical density of CsCl. (Hint: Use a modification of the result of Problem 3.3.)*

(b) The measured density is 3.99 g/cm^3. How do you explain the slight discrepancy between your calculated value and the measured one?

Solution

(a) We are asked to compute the density of CsCl. Modifying the result of Problem 3.3, we get

$$a = \frac{2r_{Cs^+} + 2r_{Cl^-}}{\sqrt{3}} = \frac{2(0.170 \text{ nm}) + 2(0.181 \text{ nm})}{\sqrt{3}}$$

$$= 0.405 \text{ nm} = 4.05 \times 10^{-8} \text{ cm}$$

From Equation 12.1

$$\rho = \frac{n'(A_{Cs} + A_{Cl})}{V_C N_A} = \frac{n'(A_{Cs} + A_{Cl})}{a^3 N_A}$$

For the CsCl crystal structure, n' = 1 formula unit/unit cell, and thus

$$\rho = \frac{(1 \text{ formula unit/unit cell})(132.91 \text{ g/mol} + 35.45 \text{ g/mol})}{(4.05 \times 10^{-8} \text{ cm})^3/\text{unit cell}(6.022 \times 10^{23} \text{ formula units/mol})}$$

$$= 4.21 \text{ g/cm}^3$$

(b) This value of the density is greater than the measured density (3.99 g/cm^3). The reason for this discrepancy is that the ionic radii in Table 12.3, used for this computation, were for a coordination number of six, when, in fact, the coordination number of both Cs^+ and Cl^- is eight. The ionic radii should be slightly greater, leading to a larger V_C value, and a lower density.

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12.19 *From the data in Table 12.3, compute the theoretical density of CaF_2, which has the fluorite structure.*

Solution

A unit cell of the fluorite structure is shown in Figure 12.5. It may be seen that there are four CaF_2 units per unit cell (i.e., $n' = 4$ formula units/unit cell). Assume that for each of the eight small cubes in the unit cell

$$a = \frac{2r_{Ca^{2+}} + 2r_{F^-}}{\sqrt{3}}$$

and, from Table 12.3

$$a = \frac{2(0.100 \text{ nm}) + 2(0.133 \text{ nm})}{\sqrt{3}} = 0.269 \text{ nm} = 2.69 \times 10^{-8} \text{ cm}$$

The volume of the unit cell is just

$$V_C = (2a)^3 = \left[(2)(2.69 \times 10^{-8} \text{ cm})\right]^3 = 1.56 \times 10^{-22} \text{ cm}^3$$

Thus, from Equation 12.1

$$\rho = \frac{n'(A_{Ca} + 2A_F)}{V_C N_A}$$

$$= \frac{(4 \text{ formula units/unit cell})\left[40.08 \text{ g/mol} + (2)(19.00 \text{ g/mol})\right]}{(1.56 \times 10^{-22} \text{ cm}^3/\text{unit cell})(6.022 \times 10^{23} \text{ formula units/mol})}$$

$$= 3.33 \text{ g/cm}^3$$

The measured density is 3.18 g/cm^3.

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12.20 *A hypothetical AX type of ceramic material is known to have a density of 2.65 g/cm^3 and a unit cell of cubic symmetry with a cell edge length of 0.43 nm. The atomic weights of the A and X elements are 86.6 and 40.3 g/mol, respectively. On the basis of this information, which of the following crystal structures is (are) possible for this material: rock salt, cesium chloride, or zinc blende? Justify your choice(s).*

Solution

We are asked to specify possible crystal structures for an AX type of ceramic material given its density (2.65 g/cm^3), that the unit cell has cubic symmetry with edge length of 0.43 nm (4.3×10^{-8} cm), and the atomic weights of the A and X elements (86.6 and 40.3 g/mol, respectively). Using Equation 12.1 and solving for n' yields

$$n' = \frac{\rho V_C N_A}{\sum A_C + \sum A_A}$$

$$= \frac{(2.65 \text{ g/cm}^3)\left[(4.30 \times 10^{-8} \text{ cm})^3/\text{unit cell}\right](6.022 \times 10^{23} \text{ formula units/mol})}{(86.6 + 40.3) \text{ g/mol}}$$

$$= 1.00 \text{ formula units/unit cell}$$

Of the three possible crystal structures, only cesium chloride has one formula unit per unit cell, and therefore, is the only possibility.

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12.21 *The unit cell for $MgFe_2O_4$ (MgO-Fe_2O_3) has cubic symmetry with a unit cell edge length of 0.836 nm. If the density of this material is 4.52 g/cm^3, compute its atomic packing factor. For this computation, you will need to use ionic radii listed in Table 12.3.*

Solution

This problem asks us to compute the atomic packing factor for $MgFe_2O_4$ given its density and unit cell edge length. It is first necessary to determine the number of formula units in the unit cell in order to calculate the sphere volume. Solving for n' from Equation 12.1 leads to

$$n' = \frac{\rho V_C N_A}{\sum A_C + \sum A_A}$$

$$= \frac{(4.52 \text{ g/cm}^3)\left[(8.36 \times 10^{-8} \text{ cm})^3/\text{unit cell}\right](6.022 \times 10^{23} \text{ formula units/mol})}{(1)(24.31 \text{ g/mol}) + (2)(55.85 \text{ g/mol}) + (4)(16.00 \text{ g/mol})}$$

$$= 8.0 \text{ formula units/unit cell}$$

Thus, in each unit cell there are 8 Mg^{2+}, 16 Fe^{3+}, and 32 O^{2-} ions. From Table 12.3, $r_{Mg^{2+}} = 0.072$ nm, $r_{Fe^{3+}} = 0.069$ nm, and $r_{O^{2-}} = 0.140$ nm. Thus, the total sphere volume in Equation 3.2 (which we denote as V_S), is just

$$V_S = (8)\left(\frac{4}{3}\pi\right)(7.2 \times 10^{-9} \text{cm})^3 + (16)\left(\frac{4}{3}\pi\right)(6.9 \times 10^{-9} \text{cm})^3$$

$$+ (32)\left(\frac{4}{3}\pi\right)(1.40 \times 10^{-8} \text{ cm})^3$$

$$= 4.02 \times 10^{-22} \text{ cm}^3$$

Now, the unit cell volume (V_C) is just

$$V_C = a^3 = (8.36 \times 10^{-8} \text{ cm})^3 = 5.84 \times 10^{-22} \text{ cm}^3$$

Finally, the atomic packing factor (APF) from Equation 3.2 is just

$$\text{APF} = \frac{V_S}{V_C} = \frac{4.02 \times 10^{-22} \text{ cm}^3}{5.84 \times 10^{-22} \text{ cm}^3} = 0.688$$

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12.22 *The unit cell for Cr_2O_3 has hexagonal symmetry with lattice parameters a = 0.4961 nm and c = 1.360 nm. If the density of this material is 5.22 g/cm^3, calculate its atomic packing factor. For this computation assume ionic radii of 0.062 nm and 0.140 nm, respectively for Cr^{3+} and O^{2-}.*

Solution

This problem asks for us to calculate the atomic packing factor for chromium oxide given values for the *a* and *c* lattice parameters, and the density. It first becomes necessary to determine the value of n' in Equation 12.1. This necessitates that we calculate the value of V_C, the unit cell volume. In Problem 3.6 it was shown that the area of the hexagonal base (AREA) is related to *a* as

$$\text{AREA} = 6R^2\sqrt{3} = 6\left(\frac{a}{2}\right)^2\sqrt{3} = 1.5a^2\sqrt{3}$$

inasmuch as, for HCP, $a = 2R$ (where *R* is the atomic radius). Now, incorporating the value of *a* provided in the problem statement into the above expression leads to

$$\text{AREA} = (1.5)(4.961 \times 10^{-8}\ \text{cm})^2(\sqrt{3}) = 6.39 \times 10^{-15}\ \text{cm}^2$$

The unit cell volume now is just

$$V_C = (\text{AREA})(c) = (6.39 \times 10^{-15}\ \text{cm}^2)(1.360 \times 10^{-7}\ \text{cm})$$

$$= 8.70 \times 10^{-22}\ \text{cm}^3$$

Now, solving for n' (Equation 12.1) yields

$$n' = \frac{\rho N_A V_C}{\sum A_C + \sum A_A}$$

$$= \frac{(5.22\ \text{g/cm}^3)(6.022 \times 10^{23}\ \text{formula units/mol})(8.70 \times 10^{-22}\ \text{cm}^3\text{/unit cell})}{(2)(52.00\ \text{g/mol}) + (3)(16.00\text{g/mol})}$$

$$= 18.0\ \text{formula units/unit cell}$$

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Or, there are 18 Cr_2O_3 units per unit cell, or 36 Cr^{3+} ions and 54 O^{2-} ions. As given in the problem statement, the radii of these two ion types are 0.062 and 0.140 nm, respectively. Thus, the total sphere volume in Equation 3.2 (which we denote as V_S), is just

$$V_S = (36)\left(\frac{4}{3}\pi\right)(r_{Cr^{3+}})^3 + (54)\left(\frac{4}{3}\pi\right)(r_{O^{2-}})^3$$

$$= (36)\left(\frac{4}{3}\pi\right)(6.2 \times 10^{-9}\,\text{cm})^3 + (54)\left(\frac{4}{3}\pi\right)(1.4 \times 10^{-8}\,\text{cm})^3$$

$$= 6.57 \times 10^{-22}\ \text{cm}^3$$

Finally, the APF is just

$$\text{APF} = \frac{V_S}{V_C} = \frac{6.57 \times 10^{-22}\ \text{cm}^3}{8.70 \times 10^{-22}\ \text{cm}^3} = 0.755$$

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12.23 *Compute the atomic packing factor for the diamond cubic crystal structure (Figure 12.15). Assume that bonding atoms touch one another, that the angle between adjacent bonds is 109.5°, and that each atom internal to the unit cell is positioned a/4 of the distance away from the two nearest cell faces (a is the unit cell edge length).*

Solution

We are asked in this problem to compute the atomic packing factor for the diamond cubic crystal structure, given that the angle between adjacent bonds is 109.5°. The first thing that we must do is to determine the unit cell volume V_C in terms of the atomic radius r. From Problem 12.15 the following relationship was developed

$$a = 4y \sin \theta$$

in which $y = 2r$ and $\theta = 35.25°$. Furthermore, since the unit cell is cubic, $V_C = a^3$; therefore

$$V_C = (4y \sin \theta)^3 = [(4)(2r)(\sin 35.25°)]^3 = 98.43\, r^3$$

Now, it is necessary to determine the sphere volume in the unit cell, V_S, in terms of r. For this unit cell (Figure 12.15) there are 4 interior atoms, 6 face atoms, and 8 corner atoms. The entirety of the interior atoms, one-half of each face atom, and one-eighth of each corner atom belong to the unit cell. Therefore, there are 8 equivalent atoms per unit cell; hence

$$V_S = (8)\left(\frac{4}{3}\pi r^3\right) = 33.51\, r^3$$

Finally, the atomic packing factor is just

$$\text{APF} = \frac{V_S}{V_C} = \frac{33.51\, r^3}{98.43\, r^3} = 0.340$$

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12.24 *Compute the atomic packing factor for cesium chloride using the ionic radii in Table 12.3 and assuming that the ions touch along the cube diagonals.*

Solution

We are asked in this problem to compute the atomic packing factor for the CsCl crystal structure. This requires that we take the ratio of the sphere volume within the unit cell and the total unit cell volume. From Figure 12.3 there is the equivalence of one Cs and one Cl ion per unit cell; the ionic radii of these two ions are 0.170 nm and 0.181 nm, respectively (Table 12.3). Thus, the sphere volume, V_S, is just

$$V_S = \frac{4}{3}(\pi)\left[(0.170\text{ nm})^3 + (0.181\text{ nm})^3\right] = 0.0454\ \text{nm}^3$$

For CsCl the unit cell edge length, a, in terms of the atomic radii is just

$$a = \frac{2r_{Cs^+} + 2r_{Cl^-}}{\sqrt{3}} = \frac{2(0.170\text{ nm}) + 2(0.181\text{ nm})}{\sqrt{3}}$$

$$= 0.405\text{ nm}$$

Since $V_C = a^3$

$$V_C = (0.405\text{ nm})^3 = 0.0664\text{ nm}^3$$

And, finally the atomic packing factor is just

$$\text{APF} = \frac{V_S}{V_C} = \frac{0.0454\text{ nm}^3}{0.0664\text{ nm}^3} = 0.684$$

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12.25 *For each of the following crystal structures, represent the indicated plane in the manner of Figures 3.11 and 3.12, showing both anions and cations:*

(a) (100) plane for the rock salt crystal structure,

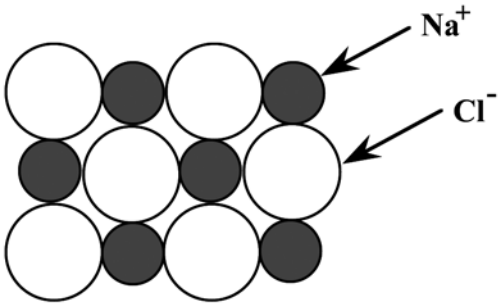
(b) (110) plane for the cesium chloride crystal structure,

(c) (111) plane for the zinc blende crystal structure, and

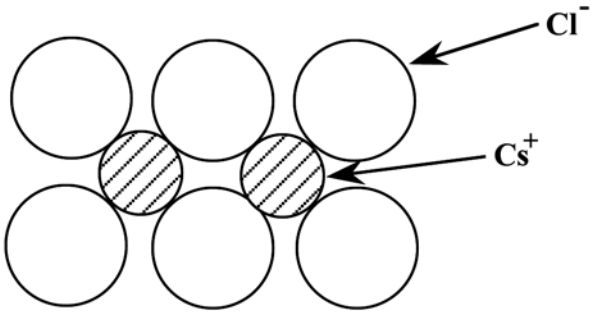
(d) (110) plane for the perovskite crystal structure.

Solution

(a) A (100) plane for the rock salt crystal structure would appear as



(b) A (110) plane for the cesium chloride crystal structure would appear as



(c) A (111) plane for the zinc blende crystal structure would appear as

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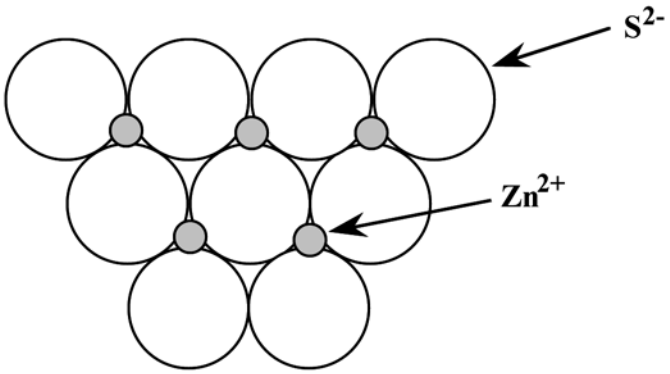
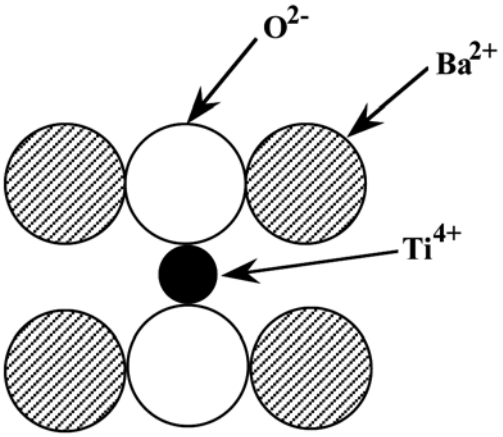


(d) A (110) plane for the perovskite crystal structure would appear as



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Silicate Ceramics

12.26 *In terms of bonding, explain why silicate materials have relatively low densities.*

Solution

The silicate materials have relatively low densities because the atomic bonds are primarily covalent in nature (Table 12.1), and, therefore, directional. This limits the packing efficiency of the atoms, and therefore, the magnitude of the density.

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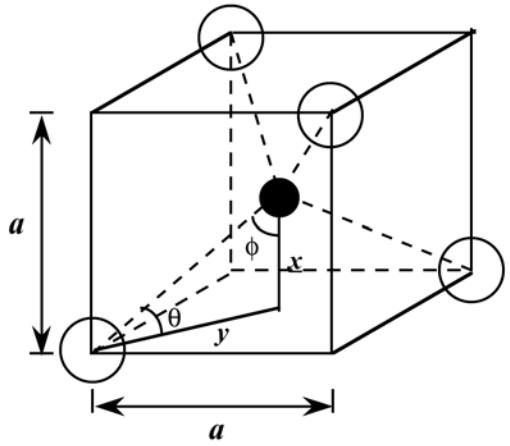
12.27 *Determine the angle between covalent bonds in an* SiO_4^{4-} *tetrahedron.*

Solution

This problem asks for us to determine the angle between covalent bonds in the SiO_4^{4-} tetrahedron. Below is shown one such tetrahedron situated within a cube.



Now if we extend the base diagonal from one corner to the other, it is the case that

$$(2y)^2 = a^2 + a^2 = 2a^2$$

or

$$y = \frac{a\sqrt{2}}{2}$$

Furthermore, $x = a/2$, and

$$\tan\theta = \frac{x}{y} = \frac{a/2}{a\sqrt{2}/2} = \frac{1}{\sqrt{2}}$$

From which

$$\theta = \tan^{-1}\left(\frac{1}{\sqrt{2}}\right) = 35.26°$$

Now, solving for the angle ϕ

$$\phi = 180° - 90° - 35.26° = 54.74°$$

Finally, the bond angle is just 2ϕ, or $2\phi = (2)(54.74°) = 109.48°$.

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Imperfections in Ceramics

12.28 *Would you expect Frenkel defects for anions to exist in ionic ceramics in relatively large concentrations? Why or why not?*

Solution

Frenkel defects for anions would not exist in appreciable concentrations because the anion is quite large and is highly unlikely to exist as an interstitial.

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12.29 *Calculate the fraction of lattice sites that are Schottky defects for sodium chloride at its melting temperature (801°C). Assume an energy for defect formation of 2.3 eV.*

Solution

We are asked in this problem to calculate the fraction of lattice sites that are Schottky defects for NaCl at its melting temperature (801°C), assuming that the energy for defect formation is 2.3 eV. In order to solve this problem it is necessary to use Equation 12.3 and solve for the N_s/N ratio. Rearrangement of this expression and substituting values for the several parameters leads to

$$\frac{N_s}{N} = \exp\left(-\frac{Q_s}{2kT}\right)$$

$$= \exp\left[-\frac{2.3 \text{ eV}}{(2)(8.62 \times 10^{-5} \text{ eV/K})(801 + 273 \text{ K})}\right]$$

$$= 4.03 \times 10^{-6}$$

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12.30 *Calculate the number of Frenkel defects per cubic meter in zinc oxide at 1000°C. The energy for defect formation is 2.51 eV, while the density for ZnO is 5.55 g/cm^3 at (1000°C).*

Solution

This problem asks that we compute the number of Frenkel defects per cubic meter in zinc oxide at 1000°C. Solution of this problem is possible using Equation 12.2. However, we must first determine the value of N, the number of lattice sites per cubic meter, which is possible using a modified form of Equation 4.2; thus

$$N = \frac{N_A \rho}{A_{Zn} + A_O}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(5.55 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{65.41 \text{ g/mol} + 16.00 \text{ g/mol}}$$

$$= 4.11 \times 10^{28} \text{ lattice sites/m}^3$$

And, finally the value of N_{fr} is computed using Equation 12.2 as

$$N_{fr} = N \exp\left(-\frac{Q_{fr}}{2kT}\right)$$

$$= (4.11 \times 10^{28} \text{ lattice sites/m}^3) \exp\left[-\frac{2.51 \text{ eV}}{(2)(8.62 \times 10^{-5} \text{ eV/K})(1000 + 273 \text{ K})}\right]$$

$$= 4.43 \times 10^{23} \text{ defects/m}^3$$

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12.31 *Using the data given below that relate to the formation of Schottky defects in some oxide ceramic (having the chemical formula MO), determine the following:*

(a) The energy for defect formation (in eV),

(b) The equilibrium number of Schottky defects per cubic meter at 1000°C, and

(c) The identity of the oxide (i.e., what is the metal M?)

T (°C)	***ρ (g/cm^3)***	***N_s (m^{-3})***
750	*5.50*	*9.21×10^{19}*
1000	*5.44*	*?*
1250	*5.37*	*5.0×10^{22}*

Solution

This problem provides for some oxide ceramic, at temperatures of 750°C and 1250°C, values for density and the number of Schottky defects per cubic meter. The (a) portion of the problem asks that we compute the energy for defect formation. To begin, let us combine a modified form of Equation 4.2 and Equation 12.3 as

$$N_s = N \exp\left(-\frac{Q_s}{2kT}\right)$$

$$= \left(\frac{N_A \rho}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT}\right)$$

Inasmuch as this is a hypothetical oxide material, we don't know the atomic weight of metal M, nor the value of Q_s in the above equation. Therefore, let us write equations of the above form for two temperatures, T_1 and T_2. These are as follows:

$$N_{s1} = \left(\frac{N_A \rho_1}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_1}\right) \qquad (12.S1a)$$

$$N_{s2} = \left(\frac{N_A \rho_2}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_2}\right) \qquad (12.S1b)$$

Dividing the first of these equations by the second leads to

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$$\frac{N_{s1}}{N_{s2}} = \frac{\left(\frac{N_A \rho_1}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_1}\right)}{\left(\frac{N_A \rho_2}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_2}\right)}$$

which, after some algebraic manipulation, reduces to the form

$$\frac{N_{s1}}{N_{s2}} = \frac{\rho_1}{\rho_2} \exp\left[-\frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \tag{12.S2}$$

Now, taking natural logarithms of both sides of this equation gives

$$\ln\left(\frac{N_{s1}}{N_{s2}}\right) = \ln\left(\frac{\rho_1}{\rho_2}\right) - \frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

and solving for Q_s leads to the expression

$$Q_s = \frac{-2k\left[\ln\left(\frac{N_{s1}}{N_{s2}}\right) - \ln\left(\frac{\rho_1}{\rho_2}\right)\right]}{\frac{1}{T_1} - \frac{1}{T_2}}$$

Let us take T_1 = 750°C and T_2 = 1250°C, and we may compute the value of Q_s as

$$Q_s = \frac{-(2)(8.62 \times 10^{-5}\ \text{eV/K})\left[\ln\left(\frac{9.2 \times 10^{19}\ \text{m}^{-3}}{5.0 \times 10^{22}\ \text{m}^{-3}}\right) - \ln\left(\frac{5.50\ \text{g/cm}^3}{5.37\ \text{g/cm}^3}\right)\right]}{\frac{1}{750 + 273\ \text{K}} - \frac{1}{1250 + 273\ \text{K}}}$$

$$= 3.40\ \text{eV}$$

(b) It is now possible to solve for N_s at 1000°C using Equation 12.S2 above. This time let's take T_1 = 1000°C and T_2 = 750°C. Thus, solving for N_{s1}, substituting values provided in the problem statement and Q_s determined above yields

$$N_{s1} = \frac{N_{s2}\,\rho_1}{\rho_2} \exp\left[-\frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

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$$= \frac{(9.2 \times 10^{19}\ \text{m}^{-3})(5.44\ \text{g/cm}^3)}{5.50\ \text{g/cm}^3} \exp\left[-\frac{3.40\ \text{eV}}{(2)(8.62 \times 10^{-5}\ \text{eV/K})}\left(\frac{1}{1000 + 273\ \text{K}} - \frac{1}{750 + 273\ \text{K}}\right)\right]$$

$$= 4.0 \times 10^{21}\ \text{m}^{-3}$$

(c) And, finally, we want to determine the identity of metal M. This is possible by computing the atomic weight of M (A_M) from Equation 12.S1a. Rearrangement of this expression leads to

$$\left(\frac{N_A \rho_1}{A_M + A_O}\right) = N_{s1} \exp\left(\frac{Q_s}{2kT_1}\right)$$

And, after further algebraic manipulation

$$\left[\frac{N_A \rho_1}{N_{s1} \exp\left(\frac{Q_s}{2kT_1}\right)}\right] = A_M + A_O$$

And, solving this expression for A_M gives

$$A_M = \left[\frac{N_A \rho_1}{N_{s1} \exp\left(\frac{Q_s}{2kT_1}\right)}\right] - A_O$$

Now, assuming that $T_1 = 750°C$, the value of A_M is

$$A_M = \left\{\frac{(6.022 \times 10^{23}\ \text{ions/mol})(5.50\ \text{g/cm}^3)(10^6\ \text{cm}^3/\text{m}^3)}{(9.2 \times 10^{19}\ \text{ions/m}^3) \exp\left[\frac{3.40\ \text{eV}}{(2)(8.62 \times 10^{-5}\ \text{eV/K})(750 + 273\ \text{K})}\right]}\right\} - 16.00\ \text{g/mol}$$

$$= 136.7\ \text{g/mol}$$

Upon consultation of the periodic table in Figure 2.6, the divalent metal (i.e., that forms M^{2+} ions) that has an atomic weight closest to 136.7 g/mol is barium. Thus, this metal oxide is BaO.

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12.32 *In your own words, briefly define the term "stoichiometric."*

Solution

Stoichiometric means having exactly the ratio of anions to cations as specified by the chemical formula for the compound.

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12.33 *If cupric oxide (CuO) is exposed to reducing atmospheres at elevated temperatures, some of the* Cu^{2+} *ions will become* Cu^{+}.

(a) Under these conditions, name one crystalline defect that you would expect to form in order to maintain charge neutrality.

(b) How many Cu^{+} *ions are required for the creation of each defect?*

(c) How would you express the chemical formula for this nonstoichiometric material?

Solution

(a) For a $Cu^{2+}O^{2-}$ compound in which a small fraction of the copper ions exist as Cu^{+}, for each Cu^{+} formed there is one less positive charge introduced (or one more negative charge). In order to maintain charge neutrality, we must either add an additional positive charge or subtract a negative charge. This may be accomplished be either creating Cu^{2+} interstitials or O^{2-} vacancies.

(b) There will be two Cu^{+} ions required for each of these defects.

(c) The chemical formula for this nonstoichiometric material is $Cu_{1+x}O$ or CuO_{1-x}, where x is some small fraction.

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12.34 *(a) Suppose that Li_2O is added as an impurity to CaO. If the Li^+ substitutes for Ca^{2+}, what kind of vacancies would you expect to form? How many of these vacancies are created for every Li^+ added?*

(b) Suppose that $CaCl_2$ is added as an impurity to CaO. If the Cl^- substitutes for O^{2-}, what kind of vacancies would you expect to form? How many of the vacancies are created for every Cl^- added?

Solution

(a) For Li^+ substituting for Ca^{2+} in CaO, oxygen vacancies would be created. For each Li^+ substituting for Ca^{2+}, one positive charge is removed; in order to maintain charge neutrality, a single negative charge may be removed. Negative charges are eliminated by creating oxygen vacancies, and for every two Li^+ ions added, a single oxygen vacancy is formed.

(b) For Cl^- substituting for O^{2-} in CaO, calcium vacancies would be created. For each Cl^- substituting for an O^{2-}, one negative charge is removed; in order to maintain charge neutrality, two Cl^- ions will lead to the formation of one calcium vacancy.

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12.35 *What point defects are possible for Al_2O_3 as an impurity in MgO? How many Al^{3+} ions must be added to form each of these defects?*

Solution

For every Al^{3+} ion that substitutes for Mg^{2+} in MgO, a single positive charge is added. Thus, in order to maintain charge neutrality, either a positive charge must be removed or a negative charge must be added.

Negative charges are added by forming O^{2-} interstitials, which are not likely to form.

Positive charges may be removed by forming Mg^{2+} vacancies, and one magnesium vacancy would be formed for every two Al^{3+} ions added.

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Ceramic Phase Diagrams

12.36 *For the ZrO_2–CaO system (Figure 12.26), write all eutectic and eutectoid reactions for cooling.*

Solution

There is only one eutectic for the portion of the ZrO_2-CaO system shown in Figure 12.26. It occurs at approximately 2250°C and 23.5 wt% CaO, and, upon cooling, the reaction is

$$\text{Liquid} \rightarrow \text{cubic } ZrO_2 + CaZrO_3$$

There are two eutectoids. One occurs at about 1000°C and about 2 wt% CaO; its reaction upon cooling is as follows:

$$\text{tetragonal} \rightarrow \text{monoclinic } ZrO_2 + \text{cubic } ZrO_2$$

The second eutectoid occurs at about 850°C and 7 wt% CaO. This reaction is

$$\text{cubic} \rightarrow \text{monoclinic } ZrO_2 + CaZr_4O_9$$

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12.37 *From Figure 12.25, the phase diagram for the MgO–Al_2O_3 system, it may be noted that the spinel solid solution exists over a range of compositions, which means that it is nonstoichiometric at compositions other than 50 mol% MgO–50 mol% Al_2O_3.*

(a) The maximum nonstoichiometry on the Al_2O_3-rich side of the spinel phase field exists at about 2000°C (3630°F) corresponding to approximately 82 mol% (92 wt%) Al_2O_3. Determine the type of vacancy defect that is produced and the percentage of vacancies that exist at this composition.

(b) The maximum nonstoichiometry on the MgO-rich side of the spinel phase field exists at about 2000°C (3630°F) corresponding to approximately 39 mol% (62 wt%) Al_2O_3. Determine the type of vacancy defect that is produced and the percentage of vacancies that exist at this composition.

Solution

(a) For this portion of the problem we are to determine the type of vacancy defect that is produced on the Al_2O_3-rich side of the spinel phase field (Figure 12.25) and the percentage of these vacancies at the maximum nonstoichiometry (82 mol% Al_2O_3). On the alumina-rich side of this phase field, there is an excess of Al^{3+} ions, which means that some of the Al^{3+} ions substitute for Mg^{2+} ions. In order to maintain charge neutrality, Mg^{2+} vacancies are formed, and for every Mg^{2+} vacancy formed, two Al^{3+} ions substitute for three Mg^{2+} ions.

Now, we will calculate the percentage of Mg^{2+} vacancies that exist at 82 mol% Al_2O_3. Let us arbitrarily choose as our basis 50 MgO-Al_2O_3 units of the stoichiometric material, which consists of 50 Mg^{2+} ions and 100 Al^{3+} ions. Furthermore, let us designate the number of Mg^{2+} vacancies as x, which means that $2x$ Al^{3+} ions have been added and $3x$ Mg^{2+} ions have been removed (two of which are filled with Al^{3+} ions). Using our 50 MgO-Al_2O_3 unit basis, the number of moles of Al_2O_3 in the nonstoichiometric material is $(100 + 2x)/2$; similarly the number of moles of MgO is $(50 - 3x)$. Thus, the expression for the mol% of Al_2O_3 is just

$$\text{mol\% } Al_2O_3 = \left[\frac{\dfrac{100 + 2x}{2}}{\dfrac{100 + 2x}{2} + (50 - 3x)} \right] \times 100$$

If we solve for x when the mol% of Al_2O_3 = 82, then x = 12.1. Thus, adding $2x$ or (2)(12.1) = 24.2 Al^{3+} ions to the original material consisting of 100 Al^{3+} and 50 Mg^{2+} ions will produce 12.1 Mg^{2+} vacancies. Therefore, the percentage of vacancies is just

$$\text{\% vacancies} = \frac{12.1}{100 + 50} \times 100 = 8.1\%$$

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(b) Now, we are asked to make the same determinations for the MgO-rich side of the spinel phase field, for 39 mol% Al_2O_3. In this case, Mg^{2+} ions are substituting for Al^{3+} ions. Since the Mg^{2+} ion has a lower charge than the Al^{3+} ion, in order to maintain charge neutrality, negative charges must be eliminated, which may be accomplished by introducing O^{2-} vacancies. For every 2 Mg^{2+} ions that substitute for 2 Al^{3+} ions, one O^{2-} vacancy is formed.

Now, we will calculate the percentage of O^{2-} vacancies that exist at 39 mol% Al_2O_3. Let us arbitrarily choose as our basis 50 MgO-Al_2O_3 units of the stoichiometric material which consists of 50 Mg^{2+} ions 100 Al^{3+} ions. Furthermore, let us designate the number of O^{2-} vacancies as y, which means that $2y$ Mg^{2+} ions have been added and $2y$ Al^{3+} ions have been removed. Using our 50 MgO-Al_2O_3 unit basis, the number of moles of Al_2O_3 in the nonstoichiometric material is $(100 - 2y)/2$; similarly the number of moles of MgO is $(50 + 2y)$. Thus, the expression for the mol% of Al_2O_3 is just

$$\text{mol\% } Al_2O_3 = \left[\frac{\dfrac{100 - 2y}{2}}{\dfrac{100 - 2y}{2} + (50 + 2y)} \right] \times 100$$

If we solve for y when the mol% of Al_2O_3 = 39, then y = 7.91. Thus, 7.91 O^{2-} vacancies are produced in the original material that had 200 O^{2-} ions. Therefore, the percentage of vacancies is just

$$\text{\% vacancies} = \frac{7.91}{200} \times 100 = 3.96\%$$

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12.38 *When kaolinite clay [$Al_2(Si_2O_5)(OH)_4$] is heated to a sufficiently high temperature, chemical water is driven off.*

(a) Under these circumstances, what is the composition of the remaining product (in weight percent Al_2O_3)?

(b) What are the liquidus and solidus temperatures of this material

Solution

(a) The chemical formula for kaolinite clay may also be written as Al_2O_3–$2SiO_2$-$2H_2O$. Thus, if we remove the chemical water, the formula becomes Al_2O_3–$2SiO_2$. The formula weight for Al_2O_3 is just (2)(26.98 g/mol) + (3)(16.00 g/mol) = 101.96 g/mol; and for SiO_2 the formula weight is 28.09 g/mol + (2)(16.00 g/mol) = 60.09 g/mol. Thus, the composition of this product, in terms of the concentration of Al_2O_3, $C_{Al_2O_3}$, in weight percent is just

$$C_{Al_2O_3} = \frac{101.96\ g/mol}{101.96\ g/mol\ +\ (2)(60.09\ g/mol)} \times 100 = 45.9\ wt\%$$

(b) The liquidus and solidus temperatures for this material as determined from the SiO_2–Al_2O_3 phase diagram, Figure 12.27, are 1825°C and 1587°C, respectively.

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Brittle Fracture of Ceramics

12.39 *Briefly explain*

(a) why there may be significant scatter in the fracture strength for some given ceramic material, and

(b) why fracture strength increases with decreasing specimen size.

Solution

(a) There may be significant scatter in the fracture strength for some given ceramic material because the fracture strength depends on the probability of the existence of a flaw that is capable of initiating a crack; this probability varies from specimen to specimen of the same material.

(b) The fracture strength increases with decreasing specimen size because as specimen size decreases, the probably of the existence of a flaw of that is capable of initiating a crack diminishes.

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12.40 *The tensile strength of brittle materials may be determined using a variation of Equation 8.1. Compute the critical crack tip radius for an Al_2O_3 specimen that experiences tensile fracture at an applied stress of 275 MPa (40,000 psi). Assume a critical surface crack length of 2×10^{-3} mm and a theoretical fracture strength of E/10, where E is the modulus of elasticity.*

Solution

We are asked for the critical crack tip radius for an Al_2O_3 material. From Equation 8.1

$$\sigma_m = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2}$$

Fracture will occur when σ_m reaches the fracture strength of the material, which is given as $E/10$; thus

$$\frac{E}{10} = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2}$$

Or, solving for ρ_t

$$\rho_t = \frac{400\ a\sigma_0^2}{E^2}$$

From Table 12.5, $E = 393$ GPa, and thus,

$$\rho_t = \frac{(400)\left(2 \times 10^{-3}\ \text{mm}\right)(275\ \text{MPa})^2}{\left(393 \times 10^3\ \text{MPa}\right)^2}$$

$$= 3.9 \times 10^{-7}\ \text{mm} = 0.39\ \text{nm}$$

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12.41 *The fracture strength of glass may be increased by etching away a thin surface layer. It is believed that the etching may alter surface crack geometry (i.e., reduce crack length and increase the tip radius). Compute the ratio of the original and etched crack tip radii for an eightfold increase in fracture strength if two-thirds of the crack length is removed.*

Solution

This problem asks that we compute the crack tip radius ratio before and after etching. Let

$$\rho_t = \text{original crack tip radius, and}$$
$$\rho_t' = \text{etched crack tip radius}$$

Also,

$$\sigma_f' = \sigma_f$$

$$a' = \frac{a}{3}$$

$$\sigma_0' = 8\sigma_0$$

Solving for $\frac{\rho_t'}{\rho_t}$ from the following

$$\sigma_f = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2} = \sigma_f' = 2\sigma_0'\left(\frac{a'}{\rho_t'}\right)^{1/2}$$

yields

$$\frac{\rho_t'}{\rho_t} = \left(\frac{\sigma_0'}{\sigma_0}\right)^2\left(\frac{a'}{a}\right) = \left(\frac{8\sigma_0}{\sigma_0}\right)^2\left(\frac{a/3}{a}\right) = 21.3$$

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Stress-Strain Behavior

12.42 *A three-point bending test is performed on a glass specimen having a rectangular cross section of height d = 5 mm (0.2 in.) and width b = 10 mm (0.4 in.); the distance between support points is 45 mm (1.75 in.).*

(a) Compute the flexural strength if the load at fracture is 290 N (65 lb_f).

(b) The point of maximum deflection Δy occurs at the center of the specimen and is described by

$$\Delta y = \frac{FL^3}{48EI}$$

where E is the modulus of elasticity and I is the cross-sectional moment of inertia. Compute Δy at a load of 266 N (60 lb_f).

Solution

(a) For this portion of the problem we are asked to compute the flexural strength for a glass specimen that is subjected to a three-point bending test. The flexural strength (Equation 12.7a) is just

$$\sigma_{fs} = \frac{3F_f L}{2bd^2}$$

for a rectangular cross-section. Using the values given in the problem statement,

$$\sigma_{fs} = \frac{(3)(290\ \text{N})(45 \times 10^{-3}\ \text{m})}{(2)(10 \times 10^{-3}\ \text{m})(5 \times 10^{-3}\ \text{m})^2} = 7.83 \times 10^7\ \text{N/m}^2 = 78.3\ \text{MPa} \quad (10{,}660\ \text{psi})$$

(b) We are now asked to compute the maximum deflection. From Table 12.5, the elastic modulus (E) for glass is 69 GPa (10×10^6 psi). Also, the moment of inertia for a rectangular cross section (Figure 12.32) is just

$$I = \frac{bd^3}{12}$$

Thus,

$$\Delta y = \frac{FL^3}{48E\left(\frac{bd^3}{12}\right)} = \frac{FL^3}{4Ebd^3}$$

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$$= \frac{(266\ \text{N})(45\ \times 10^{-3}\ \text{m})^3}{(4)(69 \times 10^9\ \text{N/m}^2)(10\ \times 10^{-3}\ \text{m})(5\ \times 10^{-3}\ \text{m})^3}$$

$$= 7.0 \times 10^{-5}\ \text{m} = 7.0 \times 10^{-2}\ \text{mm}\ \ (2.5 \times 10^{-3}\ \text{in.})$$

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12.43 *A circular specimen of MgO is loaded using a three-point bending mode. Compute the minimum possible radius of the specimen without fracture, given that the applied load is 425 N (95.5 lb_f), the flexural strength is 105 MPa (15,000 psi), and the separation between load points is 50 mm (2.0 in.).*

Solution

We are asked to calculate the maximum radius of a circular specimen of MgO that is loaded using three-point bending. Solving for R from Equation 12.7b

$$R = \left[\frac{F_f L}{\sigma_{fs}\pi}\right]^{1/3}$$

which, when substituting the parameters stipulated in the problem statement, yields

$$R = \left[\frac{(425\ \text{N})\left(50 \times 10^{-3}\ \text{m}\right)}{\left(105 \times 10^{6}\ \text{N/m}^2\right)(\pi)}\right]^{1/3}$$

$$= 4.0 \times 10^{-3}\ \text{m} = 4.0\ \text{mm}\ \ (0.16\ \text{in.})$$

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12.44 *A three-point bending test was performed on an aluminum oxide specimen having a circular cross section of radius 3.5 mm (0.14 in.); the specimen fractured at a load of 950 N (215 lb_f) when the distance between the support points was 50 mm (2.0 in.). Another test is to be performed on a specimen of this same material, but one that has a square cross section of 12 mm (0.47 in.) length on each edge. At what load would you expect this specimen to fracture if the support point separation is 40 mm (1.6 in.)?*

Solution

For this problem, the load is given at which a circular specimen of aluminum oxide fractures when subjected to a three-point bending test; we are then are asked to determine the load at which a specimen of the same material having a square cross-section fractures. It is first necessary to compute the flexural strength of the aluminum oxide, Equation 12.7b, and then, using this value, we may calculate the value of F_f in Equation 12.7a. From Equation 12.7b

$$\sigma_{fs} = \frac{F_f L}{\pi R^3}$$

$$= \frac{(950\ \text{N})(50 \times 10^{-3}\ \text{m})}{(\pi)(3.5 \times 10^{-3}\ \text{m})^3} = 352 \times 10^6\ \text{N/m}^2 = 352\ \text{MPa} \quad (50{,}000\ \text{psi})$$

Now, solving for F_f from Equation 12.7a, realizing that $b = d = 12$ mm, yields

$$F_f = \frac{2\sigma_{fs} d^3}{3L}$$

$$= \frac{(2)(352 \times 10^6\ \text{N/m}^2)(12 \times 10^{-3}\ \text{m})^3}{(3)(40 \times 10^{-3}\ \text{m})} = 10{,}100\ \text{N} \quad (2165\ \text{lb}_\text{f})$$

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12.45 (a) *A three-point transverse bending test is conducted on a cylindrical specimen of aluminum oxide having a reported flexural strength of 390 MPa (56,600 psi). If the specimen radius is 2.5 mm (0.10 in.) and the support point separation distance is 30 mm (1.2 in.), predict whether or not you would expect the specimen to fracture when a load of 620 N (140 lb_f) is applied. Justify your prediction.*

(b) Would you be 100% certain of the prediction in part (a)? Why or why not?

Solution

(a) This portion of the problem asks that we determine whether or not a cylindrical specimen of aluminum oxide having a flexural strength of 390 MPa (56,600 psi) and a radius of 2.5 mm will fracture when subjected to a load of 620 N in a three-point bending test; the support point separation is given as 30 mm. Using Equation 12.7b we will calculate the value of σ; if this value is greater than σ_{fs} (390 MPa), then fracture is expected to occur. Employment of Equation 12.7b yields

$$\sigma = \frac{FL}{\pi R^3}$$

$$= \frac{(620\text{ N})(30 \times 10^{-3}\text{ m})}{(\pi)(2.5 \times 10^{-3}\text{ m})^3} = 379 \times 10^6\text{ N/m}^2 = 379\text{ MPa} \quad (53{,}500\text{ psi})$$

Since this value is less than the given value of σ_{fs} (390 MPa), then fracture is not predicted.

(b) The certainty of this prediction is not 100% because there is always some variability in the flexural strength for ceramic materials, and since this value of σ (379 MPa) is relatively close to σ_{fs} (390 MPa) then there is some chance that fracture will occur.

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Mechanisms of Plastic Deformation

12.46 *Cite one reason why ceramic materials are, in general, harder yet more brittle than metals.*

Solution

Crystalline ceramics are harder yet more brittle than metals because they (ceramics) have fewer slip systems, and, therefore, dislocation motion is highly restricted.

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Miscellaneous Mechanical Considerations

12.47 *The modulus of elasticity for beryllium oxide (BeO) having 5 vol% porosity is 310 GPa (45 × 10^6 psi).*

(a) Compute the modulus of elasticity for the nonporous material.

(b) Compute the modulus of elasticity for 10 vol% porosity.

Solution

(a) This portion of the problem requests that we compute the modulus of elasticity for nonporous BeO given that E = 310 GPa for a material having 5 vol% porosity. Thus, we solve Equation 12.9 for E_0, using P = 0.05, which gives

$$E_0 = \frac{E}{1 - 1.9P + 0.9P^2}$$

$$= \frac{310 \text{ GPa}}{1 - (1.9)(0.05) + (0.9)(0.05)^2} = 342 \text{ GPa} \quad \left(49.6 \times 10^6 \text{ psi}\right)$$

(b) Now we are asked to determine the value of E at P = 10 vol% (i.e., 0.10). Using Equation 12.9 we get

$$E = E_0\left(1 - 1.9P + 0.9P^2\right)$$

$$= (342 \text{ GPa})\left[1 - (1.9)(0.10) + (0.9)(0.10)^2\right] = 280 \text{ GPa} \quad \left(40.6 \times 10^6 \text{ psi}\right)$$

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12.48 *The modulus of elasticity for boron carbide (B_4C) having 5 vol% porosity is 290 GPa (42×10^6 psi).*

(a) Compute the modulus of elasticity for the nonporous material.

(b) At what volume percent porosity will the modulus of elasticity be 235 GPa (34×10^6 psi)?

Solution

(a) This portion of the problem requests that we compute the modulus of elasticity for nonporous B_4C given that E = 290 GPa (42×10^6 psi) for a material having 5 vol% porosity. Thus, we solve Equation 12.9 for E_0, using $P = 0.05$, which gives

$$E_0 = \frac{E}{1 - 1.9P + 0.9P^2}$$

$$= \frac{290 \text{ GPa}}{1 - (1.9)(0.05) + (0.9)(0.05)^2} = 320 \text{ GPa} \quad \left(46.3 \times 10^6 \text{ psi}\right)$$

(b) Now we are asked to compute the volume percent porosity at which the elastic modulus of B_4C is 235 MPa (34×10^6 psi). Since from part (a), E_0 = 320 GPa, and using Equation 12.9 we get

$$\frac{E}{E_0} = \frac{235 \text{ MPa}}{320 \text{ MPa}} = 0.734 = 1 - 1.9P + 0.9P^2$$

Or

$$0.9P^2 - 1.9P + 0.266 = 0$$

Now, solving for the value of P using the quadratic equation solution yields

$$P = \frac{1.9 \pm \sqrt{(-1.9)^2 - (4)(0.9)(0.266)}}{(2)(0.9)}$$

The positive and negative roots are

$$P^+ = 1.96$$

$$P^- = 0.151$$

Obviously, only the negative root is physically meaningful, and therefore the value of the porosity to give the desired modulus of elasticity is 15.1 vol%.

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12.49 *Using the data in Table 12.5, do the following:*

(a) Determine the flexural strength for nonporous MgO assuming a value of 3.75 for n in Equation 12.10.

(b) Compute the volume fraction porosity at which the flexural strength for MgO is 62 MPa (9000 psi).

Solution

(a) This part of the problem asks us to determine the flexural strength of nonporous MgO assuming that the value of n in Equation 12.10 is 3.75. Taking natural logarithms of both sides of Equation 12.10 yields

$$\ln \sigma_{fs} = \ln \sigma_0 - nP$$

In Table 12.5 it is noted that for $P = 0.05$, $\sigma_{fs} = 105$ MPa. For the nonporous material $P = 0$ and, $\ln \sigma_0 = \ln \sigma_{fs}$. Solving for $\ln \sigma_0$ from the above equation and using these data gives

$$\ln \sigma_0 = \ln \sigma_{fs} + nP$$

$$= \ln (105 \text{ MPa}) + (3.75)(0.05) = 4.841$$

or $\sigma_0 = e^{4.841} = 127$ MPa (18,100 psi)

(b) Now we are asked to compute the volume percent porosity to yield a σ_{fs} of 62 MPa (9000 psi). Taking the natural logarithm of Equation 12.10 and solving for P leads to

$$P = \frac{\ln \sigma_0 - \ln \sigma_{fs}}{n}$$

$$= \frac{\ln (127 \text{ MPa}) - \ln (62 \text{ MPa})}{3.75}$$

$$= 0.19 \text{ or } 19 \text{ vol\%}$$

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12.50 *The flexural strength and associated volume fraction porosity for two specimens of the same ceramic material are as follows:*

σ_{fs} (*MPa*)	*P*
100	*0.05*
50	*0.20*

(a) Compute the flexural strength for a completely nonporous specimen of this material.

(b) Compute the flexural strength for a 0.10 volume fraction porosity.

Solution

(a) Given the flexural strengths at two different volume fraction porosities, we are asked to determine the flexural strength for a nonporous material. If the natural logarithm is taken of both sides of Equation 12.10, then

$$\ln \sigma_{fs} = \ln \sigma_0 - nP$$

Using the data provided in the problem statement, two simultaneous equations may be written as

$$\ln (100 \text{ MPa}) = \ln \sigma_0 - (0.05)n$$

$$\ln (50 \text{ MPa}) = \ln \sigma_0 - (0.20)n$$

Solving for n and σ_0 leads to $n = 4.62$ and $\sigma_0 = 126$ MPa. For the nonporous material, $P = 0$, and, from Equation 12.10, $\sigma_0 = \sigma_{fs}$. Thus, σ_{fs} for $P = 0$ is 126 MPa.

(b) Now, we are asked for σ_{fs} at $P = 0.10$ for this same material. Utilizing Equation 12.10 yields

$$\sigma_{fs} = \sigma_0 \exp(-nP)$$

$$= (126 \text{ MPa}) \exp\left[-(4.62)(0.10)\right]$$

$$= 79.4 \text{ MPa}$$

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DESIGN PROBLEMS

Crystal Structures

12.D1 *Gallium arsenide (GaAs) and gallium phosphide (GaP) both have the zinc blende crystal structure and are soluble in one another at all concentrations. Determine the concentration in weight percent of GaP that must be added to GaAs to yield a unit cell edge length of 0.5570 nm. The densities of GaAs and GaP are 5.316 and 4.130 g/cm^3, respectively.*

Solution

This problem asks that we determine the concentration (in weight percent) of GaP that must be added to GaAs to yield a unit cell edge length of 0.5570 nm. The densities of GaAs and GaP were given in the problem as 5.307 and 4.130 g/cm^3, respectively. To begin, it is necessary to employ Equation (13.1), and solve for the unit cell volume, V_C, for the GaP-GaAs alloy as

$$V_C = \frac{n' A_{ave}}{\rho_{ave} N_A}$$

where A_{ave} and ρ_{ave} are the atomic weight and density, respectively, of the InAs-GaAs alloy. Inasmuch as both of these materials have the zinc blende crystal structure, which has cubic symmetry, V_C is just the cube of the unit cell length, a. That is

$$V_C = a^3 = (0.5570 \text{ nm})^3$$

$$= (5.570 \times 10^{-8} \text{ cm})^3 = 1.728 \times 10^{-22} \text{ cm}^3$$

It is now necessary to construct expressions for A_{ave} and ρ_{ave} in terms of the concentration of indium arsenide, C_{InAs} using Equations 4.11a and 4.10a. For A_{ave} we have

$$A_{ave} = \frac{100}{\frac{C_{GaP}}{A_{GaP}} + \frac{(100 - C_{GaP})}{A_{GaAs}}}$$

$$= \frac{100}{\frac{C_{GaP}}{100.69 \text{ g/mol}} + \frac{(100 - C_{GaP})}{144.64 \text{ g/mol}}}$$

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whereas for ρ_{ave}

$$\rho_{ave} = \frac{100}{\frac{C_{GaP}}{\rho_{GaP}} + \frac{(100 - C_{GaP})}{\rho_{GaAs}}}$$

$$= \frac{100}{\frac{C_{GaP}}{4.130\ g/cm^3} + \frac{(100 - C_{GaP})}{5.316\ g/cm^3}}$$

Within the zinc blende unit cell there are four formula units, and thus, the value of n' in Equation 12.1 is 4; hence, this expression may be written in terms of the concentration of GaP in weight percent as follows:

$$V_C = 1.728 \times 10^{-22}\ cm^3$$

$$= \frac{n' A_{ave}}{\rho_{ave} N_A}$$

$$= \frac{(4\ \text{formula units/unit cell})\left[\frac{100}{\frac{C_{GaP}}{100.69\ g/mol} + \frac{(100 - C_{GaP})}{144.64\ g/mol}}\right]}{\left[\frac{100}{\frac{C_{GaP}}{4.130\ g/cm^3} + \frac{(100 - C_{GaP})}{5.316\ g/cm^3}}\right](6.022 \times 10^{23}\ \text{formula units/mol})}$$

And solving this expression for C_{GaP} leads to $C_{GaP} = 33.7$ wt%.

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Stress-Strain Behavior

12.D2 *It is necessary to select a ceramic material to be stressed using a three-point loading scheme (Figure 12.32). The specimen must have a circular cross section and a radius of 2.5 mm (0.10 in.), and must not experience fracture or a deflection of more than 6.2×10^{-2} mm (2.4×10^{-3} in.) at its center when a load of 275 N (62 lb_f) is applied. If the distance between support points is 45 mm (1.77 in.), which of the materials in Table 12.5 are candidates? The magnitude of the centerpoint deflection may be computed using the equation supplied in Problem 12.42.*

Solution

This problem asks for us to determine which of the ceramic materials in Table 12.5, when fabricated into cylindrical specimens and stressed in three-point loading, will not fracture when a load of 275 N (62 lb_f) is applied, and also will not experience a center-point deflection of more than 6.2×10^{-2} mm (2.4×10^{-3} in.). The first of these criteria is met by those materials that have flexural strengths greater than the stress calculated using Equation 12.7b. According to this expression

$$\sigma_{fs} = \frac{FL}{\pi R^3}$$

$$= \frac{(275\ \text{N})(45 \times 10^{-3}\ \text{m})}{(\pi)(2.5 \times 10^{-3}\ \text{m})^3} = 252 \times 10^6\ \text{N/m}^2 = 252\ \ \text{MPa}\ (35{,}000\ \text{psi})$$

Of the materials in Table 12.5, the following have flexural strengths greater than this value: Si_3N_4, ZrO_2, SiC, and Al_2O_3

For the second criterion we must solve for the magnitude of the modulus of elasticity, *E*, from the equation given in Problem 12.42 where the expression for the cross-sectional moment of inertia appears in Figure 12.32; that is, for a circular cross-section $I = \frac{\pi R^4}{4}$. Solving for *E* from these two expressions

$$E = \frac{FL^3}{12\pi R^4 \Delta y}$$

$$= \frac{(275\ \text{N})(45 \times 10^{-3}\ \text{m})^3}{(12)(\pi)(2.5 \times 10^{-3}\ \text{m})^4(6.2 \times 10^{-5}\ \text{m})}$$

$$= 274 \times 10^9\ \text{N/m}^2 = 274\ \text{GPa}\ (38 \times 10^6\ \text{psi})$$

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Of those materials that satisfy the first criterion, only Al_2O_3, Si_3N_4, and SiC have moduli of elasticity greater than this value (Table 12.5), and, therefore, are possible candidates.

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CHAPTER 13

APPLICATIONS AND PROCESSING OF CERAMICS

PROBLEM SOLUTIONS

Glasses
Glass-Ceramics

13.1 *Cite the two desirable characteristics of glasses.*

Solution

Two desirable characteristics of glasses are optical transparency and ease of fabrication.

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13.2 *(a) What is crystallization?*

(b) Cite two properties that may be improved by crystallization.

Solution

(a) Crystallization is the process whereby a glass material is caused to transform to a crystalline solid, usually as a result of a heat treatment.

(b) Two properties that may be improved by crystallization are (1) a lower coefficient of thermal expansion, and (2) higher strength.

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Refractories

13.3 *For refractory ceramic materials, cite three characteristics that improve with and two characteristics that are adversely affected by increasing porosity.*

Solution

For refractory ceramic materials, three characteristics that improve with increasing porosity are (1) decreased thermal expansion and contraction upon thermal cycling, (2) improved thermal insulation, and (3) improved resistance to thermal shock. Two characteristics that are adversely affected are (1) load-bearing capacity and (2) resistance to attack by corrosive materials.

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13.4 *Find the maximum temperature to which the following two magnesia–alumina refractory materials may be heated before a liquid phase will appear.*

(a) A spinel-bonded alumina material of composition 95 wt% Al_2O_3-5 wt% MgO.

(b) A magnesia-alumina spinel of composition 65 wt% Al_2O_3-35 wt% MgO.

Consult Figure 12.25.

Solution

(a) From Figure 12.25, for a spinel-bonded magnesia material (95 wt% Al_2O_3-5 wt% MgO), the maximum temperature without a liquid phase corresponds to the temperature of the eutectic isotherm on the Al_2O_3-rich side of the phase diagram, which is approximately 2000°C (3630°F).

(b) The maximum temperature without the formation of a liquid phase for a magnesia-alumina spinel (65 wt% Al_2O_3-35 wt% MgO) lies at the phase boundary between $MgAl_2O_4$(ss)-$MgAl_2O_4$ + Liquid phase fields (just slightly to the left of the congruent melting point at which the two phase boundaries become tangent); this temperature is approximately 2030°C (3685°F).

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13.5 *Upon consideration of the SiO_2–Al_2O_3 phase diagram, Figure 12.27, for each pair of the following list of compositions, which would you judge to be the more desirable refractory? Justify your choices.*

(a) 20 wt% Al_2O_3-80 wt% SiO_2 and 25 wt% Al_2O_3-75 wt% SiO_2

(b) 70 wt% Al_2O_3-30 wt% SiO_2 and 80 wt% Al_2O_3-20 wt% SiO_2

Solution

(a) The 25 wt% Al_2O_3-75 wt% SiO_2 will be more desirable because the liquidus temperature will be greater for this composition; therefore, at any temperature within the mullite + liquid region on the phase diagram, there will be a lower fraction of the liquid phase present than for the 20 wt% Al_2O_3-80 wt% SiO_2 composition, and, thus, the mechanical integrity will be greater.

(b) The 80 wt% Al_2O_3-20 wt% SiO_2 composition will be more desirable because, for this composition, a liquid phase does not form until about 1890°C, whereas, for the 70 wt% Al_2O_3-30 wt% SiO_2 material, a liquid phase forms at a much lower temperature--1587°C.

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13.6 *Compute the mass fractions of liquid in the following refractory materials at 1600°C (2910°F):*

(a) 6 wt% Al_2O_3-94 wt% SiO_2

(b) 10 wt% Al_2O_3-90 wt% SiO_2

(c) 30 wt% Al_2O_3-70 wt% SiO_2

(d) 80 wt% Al_2O_3-20 wt% SiO_2

Solution

This problem calls for us to compute the mass fractions of liquid for two fireclay refractory materials at 1600°C. In order to solve this problem it is necessary that we use the SiO_2-Al_2O_3 phase diagram (Figure 12.27) in conjunction with tie-lines and the lever rule at 1600°C.

(a) For the 6 wt% Al_2O_3-94 wt% SiO_2 composition, the appropriate lever-rule expression is

$$W_L = \frac{C_0 - C_{SiO_2}}{C_L - C_{SiO_2}}$$

For a tie-line constructed across the SiO_2-Liquid phase field at 1600°C

C_L = 7 wt% Al_2O_3

C_{SiO_2} = 0 wt% Al_2O_3

And, inasmuch as C_0 = 6 wt% Al_2O_3 the mass fraction of liquid using the above lever-rule expression is

$$W_L = \frac{6 - 0}{7 - 0} = 0.86$$

(b) For the 10 wt% Al_2O_3-90 wt% SiO_2 composition, the appropriate lever-rule expression is

$$W_L = \frac{C_{mullite} - C_0}{C_{mullite} - C_L}$$

For a tie-line constructed across the Mullite (ss)-Liquid phase field at 1600°C

$C_{mullite}$ = 72 wt% Al_2O_3

C_L = 8 wt% Al_2O_3

And, inasmuch as C_0 = 10 wt% Al_2O_3 the mass fraction of liquid using the above lever-rule expression is

$$W_L = \frac{72 - 10}{72 - 8} = 0.97$$

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(c) For the 30 wt% Al_2O_3-70 wt% SiO_2 composition, the appropriate lever-rule expression is

$$W_L = \frac{C_{\text{mullite}} - C_0}{C_{\text{mullite}} - C_L}$$

For a tie-line constructed across the Mullite (ss)-Liquid phase field at 1600°C

C_{mullite} = 72 wt% Al_2O_3

C_L = 8 wt% Al_2O_3

And, inasmuch as C_0 = 30 wt% Al_2O_3 the mass fraction of liquid using the above lever-rule expression is

$$W_L = \frac{72 - 30}{72 - 8} = 0.66$$

(d) For the 80 wt% Al_2O_3-20 wt% SiO_2 composition at 1600°C, only alumina and mullite phases are present; thus $W_L = 0$.

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13.7 *For the $MgO–Al_2O_3$ system, what is the maximum temperature that is possible without the formation of a liquid phase? At what composition or over what range of compositions will this maximum temperature be achieved?*

Solution

This problem asks that we specify, for the $MgO\text{-}Al_2O_3$ system, Figure 12.25, the maximum temperature without the formation of a liquid phase; it is approximately 2800°C which is possible for pure MgO.

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Cements

13.8 *Compare the manner in which the aggregate particles become bonded together in clay-based mixtures during firing and in cements during setting.*

Solution

For clay-based aggregates, a liquid phase forms during firing, which infiltrates the pores between the unmelted particles; upon cooling, this liquid becomes a glass, that serves as the bonding phase.

With cements, the bonding process is a chemical, hydration reaction between the water that has been added and the various cement constituents. The cement particles are bonded together by reactions that occur at the particle surfaces.

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Fabrication and Processing of Glasses and Glass-Ceramics

13.9 *Soda and lime are added to a glass batch in the form of soda ash (Na_2CO_3) and limestone ($CaCO_3$). During heating, these two ingredients decompose to give off carbon dioxide (CO_2), the resulting products being soda and lime. Compute the weight of soda ash and limestone that must be added to 100 lb_m of quartz (SiO_2) to yield a glass of composition 75 wt% SiO_2, 15 wt% Na_2O, and 10 wt% CaO.*

Solution

We are asked to compute the weight of soda ash and limestone that must be added to 100 lb_m of SiO_2 to yield a glass composition of 75 wt% SiO_2, 15 wt% Na_2O, and 10 wt% CaO. Let x equal the weight of Na_2O and y equal the weight of CaO. Then, employment of a modified form Equation 4.3, we may write the following expressions for the concentrations of Na_2O (C_{Na_2O}) and CaO (C_{CaO}):

$$C_{Na_2O} = 15 \text{ wt\%} = \frac{x}{100 + x + y} \times 100$$

$$C_{CaO} = 10 \text{ wt\%} = \frac{y}{100 + x + y} \times 100$$

Solving for x and y from these two expressions yields $x = 20.0$ lb_m Na_2O and $y = 13.3$ lb_m CaO.

Now, in order to compute the weights of Na_2CO_3 and $CaCO_3$, we must employ molecular weights. The molecular weights of Na_2CO_3 ($MW_{Na_2CO_3}$) and Na_2O (MW_{Na_2O}) are as follows:

$$MW_{Na_2CO_3} = 2(A_{Na}) + A_C + 3(A_O)$$

$$= 2(22.99 \text{ g/mol}) + 12.01 \text{ g/mol} + 3(16.00 \text{g/mol}) = 105.99 \text{ g/mol}$$

$$MW_{Na_2O} = 2(A_{Na}) + A_O$$

$$= 2(22.99 \text{ g/mol}) + 16.00 \text{ g/mol} = 61.98 \text{ g/mol}$$

And, finally, the mass of Na_2CO_3 ($m_{Na_2CO_3}$) is equal to

$$m_{Na_2CO_3} = (20.0 \text{ lb}_m)\left(\frac{MW_{Na_2CO_3}}{MW_{Na_2O}}\right)$$

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$$= (20.0\ \text{lb}_\text{m})\left(\frac{105.99\ \text{g/mol}}{61.98\ \text{g/mol}}\right) = 34.2\ \text{lb}_\text{m}$$

Likewise, the molecular weights of $CaCO_3$ (MW_{CaCO_3}) and CaO (MW_{CaO}) are as follows:

$$MW_{CaCO_3} = A_{Ca} + A_C + 3(A_O)$$

$$= 40.08\ \text{g/mol} + 12.01\ \text{g/mol} + (3)(16.00\ \text{g/mol}) = 100.09\ \text{g/mol}$$

$$MW_{CaO} = A_{Ca} + A_O$$

$$= 40.08\ \text{g/mol} + 16.00\ \text{g/mol} = 56.08\ \text{g/mol}$$

Such that the mass of $CaCO_3$ (m_{CaCO_3}) is equal to

$$m_{CaCO_3} = (13.3\ \text{lb}_\text{m})\left(\frac{MW_{CaCO_3}}{MW_{CaO}}\right)$$

$$= (13.3\ \text{lb}_\text{m})\left(\frac{100.09\ \text{g/mol}}{56.08\ \text{g/mol}}\right) = 23.7\ \text{lb}_\text{m}$$

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13.10 *What is the distinction between glass transition temperature and melting temperature?*

Solution

The glass transition temperature is, for a noncrystalline ceramic, that temperature at which there is a change of slope for the specific volume versus temperature curve (Figure 13.6).

The melting temperature is, for a crystalline material and upon cooling, that temperature at which there is a sudden and discontinuous decrease in the specific-volume-versus-temperature curve.

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13.11 *Compare the temperatures at which soda–lime, borosilicate, 96% silica, and fused silica may be annealed.*

Solution

The annealing point is that temperature at which the viscosity of the glass is 10^{12} Pa-s (10^{13} P). From Figure 13.7, these temperatures for the several glasses are as follows:

Glass	Annealing Temperature
Soda-lime	500°C (930°F)
Borosilicate	565°C (1050°F)
96% Silica	930°C (1705°F)
Fused silica	1170°C (2140°F)

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13.12 *Compare the softening points for 96% silica, borosilicate, and soda–lime glasses.*

Solution

The softening point of a glass is that temperature at which the viscosity is 4×10^6 Pa-s; from Figure 13.7, these temperatures for the 96% silica, borosilicate, and soda-lime glasses are 1540°C (2800°F), 830°C (1525°F), and 700°C (1290°F), respectively.

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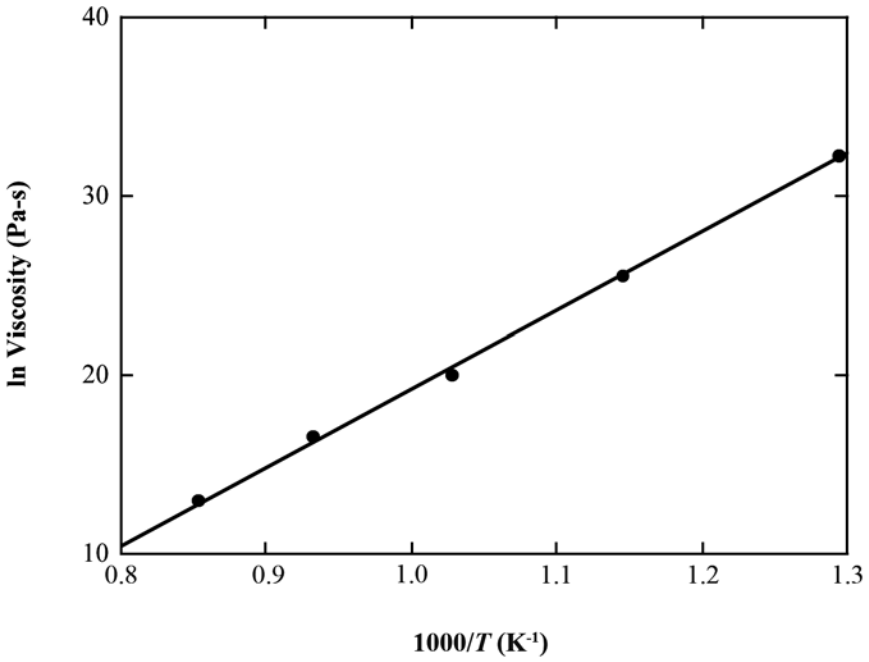
13.13 *The viscosity η of a glass varies with temperature according to the relationship*

$$\eta = A \exp\left(\frac{Q_{\text{vis}}}{RT}\right)$$

where Q_{vis} is the energy of activation for viscous flow, A is a temperature-independent constant, and R and T are, respectively, the gas constant and the absolute temperature. A plot of ln η versus l/T should be nearly linear, and with a slope of Q_{vis}/R. Using the data in Figure 13.7, (a) make such a plot for the borosilicate glass, and (b) determine the activation energy between temperatures of 500 and 900°C.

Solution

(a) Below is shown the logarithm viscosity versus reciprocal of temperature plot for the borosilicate glass, using the data in Figure 13.7. The dashed line has been drawn through the data points corresponding to temperatures between 500 and 900ºC (as stipulated in the problem statement).



(b) The activation energy, Q_{vis}, may be computed according to

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$$Q_{vis} = R\left[\frac{\Delta \ln \eta}{\Delta\left(\frac{1}{T}\right)}\right] = R\left(\frac{\ln \eta_1 - \ln \eta_2}{\frac{1}{T_1} - \frac{1}{T_2}}\right)$$

where R is the gas constant, and $\frac{\Delta \ln \eta}{\Delta\left(\frac{1}{T}\right)}$ is the slope of the dashed line that has been constructed. Taking $1/T_1$ and $1/T_2$ as 0.8×10^{-3} and 1.3×10^{-3} K^{-1}, respectively, then the corresponding values of $\ln \eta_1$ and $\ln \eta_2$ are 10.59 and 32.50. Therefore,

$$Q_{vis} = R\left(\frac{\ln \eta_1 - \ln \eta_2}{\frac{1}{T_1} - \frac{1}{T_2}}\right) = (8.31 \text{ J/mol} - \text{K})\left(\frac{10.59 - 32.50}{0.8 \times 10^{-3} \text{ K}^{-1} - 1.3 \times 10^{-3} \text{ K}^{-1}}\right)$$

$$= 364{,}000 \text{ J/mol}$$

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13.14 *For many viscous materials, the viscosity η may be defined in terms of the expression*

$$\eta = \frac{\sigma}{d\varepsilon/dt}$$

where σ and dε/dt are, respectively, the tensile stress and the strain rate. A cylindrical specimen of a soda-lime glass of diameter 5 mm (0.2 in.) and length 100 mm (4 in.) is subjected to a tensile force of 1 N (0.224 lb_f) along its axis. If its deformation is to be less than 1 mm (0.04 in.) over a week's time, using Figure 13.7, determine the maximum temperature to which the specimen may be heated.

Solution

This problem calls for us to determine the maximum temperature to which a cylindrical specimen of soda-lime glass may be heated in order that its deformation be less than 1 mm over a week's time. According to Equation 6.1

$$\sigma = \frac{F}{A_0} = \frac{1\ \text{N}}{\pi\left(\frac{5 \times 10^{-3}\ \text{m}}{2}\right)^2} = 5.09 \times 10^4\ \text{Pa}$$

Also,

$$\frac{d\varepsilon}{dt} = \frac{d\left(\frac{\Delta l}{l_0}\right)}{dt}$$

$$= \frac{1\ \text{mm}/100\ \text{mm}}{(1\ \text{wk})(7\ \text{days/week})(24\ \text{h/day})(3600\ \text{s/h})} = 1.653 \times 10^{-8}\ \text{s}^{-1}$$

Thus,

$$\eta = \frac{\sigma}{d\varepsilon/dt} = \frac{5.09 \times 10^4\ \text{Pa}}{1.653 \times 10^{-8}\ \text{s}^{-1}} = 3.1 \times 10^{12}\ \text{Pa-s}$$

From Figure 13.7, the temperature at which the viscosity of the soda-lime glass is 3.1×10^{12} Pa-s is about 500°C (930°F).

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13.15 *(a) Explain why residual thermal stresses are introduced into a glass piece when it is cooled.*

(b) Are thermal stresses introduced upon heating? Why or why not?

Solution

(a) Residual thermal stresses are introduced into a glass piece when it is cooled because surface and interior regions cool at different rates, and, therefore, contract different amounts; since the material will experience very little, if any deformation, stresses are established.

(b) Yes, thermal stresses will be introduced because of thermal expansion upon heating for the same reason as for thermal contraction upon cooling.

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13.16 *Borosilicate glasses and fused silica are resistant to thermal shock. Why is this so?*

Solution

Borosilicate glasses and fused silica are resistant to thermal shock because they have relatively low coefficients of thermal expansion; therefore, upon heating or cooling, the difference in the degree of expansion or contraction across a cross-section of a ware that is constructed from these materials will be relatively low.

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13.17 *In your own words, briefly describe what happens as a glass piece is thermally tempered.*

Thermal tempering of glasses is described in Section 13.9.

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13.18 *Glass pieces may also be strengthened by chemical tempering. With this procedure, the glass surface is put in a state of compression by exchanging some of the cations near the surface with other cations having a larger diameter. Suggest one type of cation that, by replacing Na^+, will induce chemical tempering in a soda–lime glass.*

Solution

Chemical tempering will be accomplished by substitution, for Na^+, another monovalent cation with a slightly larger diameter. From Table 12.3, both K^+ and Cs^+ fill these criteria, having ionic radii of 0.138 and 0.170 nm, respectively, which are larger than the ionic radius of Na^+ (0.102 nm). In fact, soda-lime glasses are tempered by a K^+-Na^+ ion exchange.

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Fabrication and Processing of Clay Products

13.19 *Cite the two desirable characteristics of clay minerals relative to fabrication processes.*

Solution

Two desirable characteristics of clay minerals relative to fabrication processes are (1) they become hydroplastic (and therefore formable) when mixed with water; and (2) during firing, clays melt over a range of temperatures, which allows some fusion and bonding of the ware without complete melting and a loss of mechanical integrity and shape.

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13.20 *From a molecular perspective, briefly explain the mechanism by which clay minerals become hydroplastic when water is added.*

Solution

Clays become hydroplastic when water is added because the water molecules occupy regions between the layered molecular sheets; these water molecules essentially eliminate the secondary molecular bonds between adjacent sheets, and also form a thin film around the clay particles. The net result is that the clay particles are relatively free to move past one another, which is manifested as the hydroplasticity phenomenon.

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13.21 *(a) What are the three main components of a whiteware ceramic such as porcelain?*

(b) What role does each component play in the forming and firing procedures?

Solution

(a) The three components of a whiteware ceramic are clay, quartz, and a flux.

(b) With regard to the role that each component plays:

Quartz acts as a filler material.

Clay facilitates the forming operation since, when mixed with water, the mass may be made to become either hydroplastic or form a slip. Also, since clays melt over a range of temperatures, the shape of the piece being fired will be maintained.

The flux facilitates the formation of a glass having a relatively low melting temperature.

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13.22 *(a) Why is it so important to control the rate of drying of a ceramic body that has been hydroplastically formed or slip cast?*

(b) Cite three factors that influence the rate of drying, and explain how each affects the rate.

Solution

(a) It is important to control the rate of drying inasmuch as if the rate of drying is too rapid, there will be nonuniform shrinkage between surface and interior regions, such that warping and/or cracking of the ceramic ware may result.

(b) Three factors that affect the rate of drying are temperature, humidity, and rate of air flow. The rate of drying is enhanced by increasing both the temperature and rate of air flow, and by decreasing the humidity of the air.

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13.23 *Cite one reason why drying shrinkage is greater for slip cast or hydroplastic products that have smaller clay particles.*

Solution

The reason that drying shrinkage is greater for products having smaller clay particles is because there is more particle surface area, and, consequently, more water will surround a given volume of particles. The drying shrinkage will thus be greater as this water is removed, and as the interparticle separation decreases.

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13.24 *(a) Name three factors that influence the degree to which vitrification occurs in clay-based ceramic wares.*

(b) Explain how density, firing distortion, strength, corrosion resistance, and thermal conductivity are affected by the extent of vitrification.

Solution

(a) Three factors that influence the degree to which vitrification occurs in clay-based ceramic wares are: (1) composition (especially the concentration of flux present); (2) the temperature of firing; and (3) the time at the firing temperature.

(b) Density will increase with degree of vitrification since the total remaining pore volume decreases.

Firing distortion will increase with degree of vitrification since more liquid phase will be present at the firing temperature.

Strength will also increase with degree of vitrification inasmuch as more of the liquid phase forms, which fills in a greater fraction of pore volume. Upon cooling, the liquid forms a glass matrix of relatively high strength.

Corrosion resistance normally increases also, especially at service temperatures below that at which the glass phase begins to soften. The rate of corrosion is dependent on the amount of surface area exposed to the corrosive medium; hence, decreasing the total surface area by filling in some of the surface pores, diminishes the corrosion rate.

Thermal conductivity will increase with degree of vitrification. The glass phase has a higher conductivity than the pores that it has filled.

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Powder Pressing

13.25 *Some ceramic materials are fabricated by hot isostatic pressing. Cite some of the limitations and difficulties associated with this technique.*

Solution

The principal disadvantage of hot-isostatic pressing is that it is expensive. The pressure is applied on a pre-formed green piece by a gas. Thus, the process is slow, and the equipment required to supply the gas and withstand the elevated temperature and pressure is costly.

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DESIGN PROBLEM

13.D1 *Some of our modern kitchen cookware is made of ceramic materials.*

(a) List at least three important characteristics required of a material to be used for this application.

(b) Make a comparison of three ceramic materials as to their relative properties and, in addition, to cost.

(c) On the basis of this comparison, select the material most suitable for the cookware.

Solution

(a) Important characteristics that are required of a ceramic material to be used for kitchen cookware are: (1) it must have a high resistance to thermal shock (Section 19.5) in order to withstand relatively rapid changes in temperature; (2) it must have a relatively high thermal conductivity; 3) it must be relatively strong and tough in order to endure normal kitchen use; and 4) it must be nontoxic.

(b) Possible materials worth considering are a common soda-lime glass, a borosilicate (Pyrex) glass, and a glass ceramic. These materials and some of their characteristics are discussed in this chapter. Using Equation 17.9 a comparison of the resistance to thermal shock may be made. The student will need to obtain cost information.

(c) It is left to the student to make this determination and justify the decision.

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CHAPTER 14

POLYMER STRUCTURES

PROBLEM SOLUTIONS

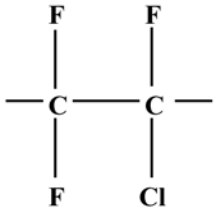
Hydrocarbon Molecules
Polymer Molecules
The Chemistry of Polymer Molecules

14.1 *On the basis of the structures presented in this chapter, sketch repeat unit structures for the following polymers: (a) polychlorotrifluoroethylene, and (b) poly(vinyl alcohol).*

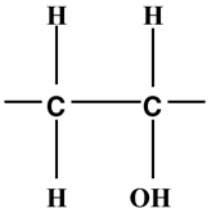
Solution

The repeat unit structures called for are sketched below.

(a) Polychlorotrifluoroethylene



(b) Poly(vinyl alcohol)



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Molecular Weight

14.2 *Compute repeat unit molecular weights for the following: (a) poly(vinyl chloride), (b) poly(ethylene terephthalate), (c) polycarbonate, and (d) polydimethylsiloxane.*

Solution

(a) For poly(vinyl chloride), each repeat unit consists of two carbons, three hydrogens, and one chlorine (Table 14.3). If A_C, A_H and A_{Cl} represent the atomic weights of carbon, hydrogen, and chlorine, respectively, then

$$m = 2(A_C) + 3(A_H) + (A_{Cl})$$

$$= (2)(12.01 \text{ g/mol}) + (3)(1.008 \text{ g/mol}) + 35.45 \text{ g/mol} = 62.49 \text{ g/mol}$$

(b) For poly(ethylene terephthalate), from Table 14.3, each repeat unit has ten carbons, eight hydrogens, and four oxygens. Thus,

$$m = 10(A_C) + 8(A_H) + 4(A_O)$$

$$= (10)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) + (4)(16.00 \text{ g/mol}) = 192.16 \text{ g/mol}$$

(c) For polycarbonate, from Table 14.3, each repeat unit has sixteen carbons, fourteen hydrogens, and three oxygens. Thus,

$$m = 16(A_C) + 14(A_H) + 3(A_O)$$

$$= (16)(12.01 \text{ g/mol}) + (14)(1.008 \text{ g/mol}) + (3)(16.00 \text{ g/mol})$$

$$= 254.27 \text{ g/mol}$$

(d) For polydimethylsiloxane, from Table 14.5, each repeat unit has two carbons, six hydrogens, one silicon and one oxygen. Thus,

$$m = 2(A_C) + 6(A_H) + (A_{Si}) + (A_O)$$

$$= (2)(12.01 \text{ g/mol}) + (6)(1.008 \text{ g/mol}) + (28.09 \text{ g/mol}) + (16.00 \text{ g/mol}) = 74.16 \text{ g/mol}$$

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14.3 *The number-average molecular weight of a polypropylene is 1,000,000 g/mol. Compute the degree of polymerization.*

Solution

We are asked to compute the degree of polymerization for polypropylene, given that the number-average molecular weight is 1,000,000 g/mol. The repeat unit molecular weight of polypropylene is just

$$m = 3(A_C) + 6(A_H)$$

$$= (3)(12.01 \text{ g/mol}) + (6)(1.008 \text{ g/mol}) = 42.08 \text{ g/mol}$$

Now it is possible to compute the degree of polymerization using Equation 14.6 as

$$DP = \frac{\overline{M}_n}{m} = \frac{1,000,000 \text{ g/mol}}{42.08 \text{ g/mol}} = 23,760$$

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14.4 *(a) Compute the repeat unit molecular weight of polystyrene.*

(b) Compute the number-average molecular weight for a polystyrene for which the degree of polymerization is 25,000.

Solution

(a) The repeat unit molecular weight of polystyrene is called for in this portion of the problem. For polystyrene, from Table 14.3, each repeat unit has eight carbons and eight hydrogens. Thus,

$$m = 8(A_C) + 8(A_H)$$

$$= (8)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 104.14 \text{ g/mol}$$

(b) We are now asked to compute the number-average molecular weight. Since the degree of polymerization is 25,000, using Equation 14.6

$$\overline{M}_n = (DP)m = (25,000)(104.14 \text{ g/mol}) = 2.60 \times 10^6 \text{ g/mol}$$

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14.5 *Below, molecular weight data for a polypropylene material are tabulated. Compute (a) the number-average molecular weight, (b) the weight-average molecular weight, and (c) the degree of polymerization.*

Molecular Weight Range (g/mol)	x_i	w_i
8,000–16,000	*0.05*	*0.02*
16,000–24,000	*0.16*	*0.10*
24,000–32,000	*0.24*	*0.20*
32,000–40,000	*0.28*	*0.30*
40,000–48,000	*0.20*	*0.27*
48,000–56,000	*0.07*	*0.11*

Solution

(a) From the tabulated data, we are asked to compute $\overline{M}_n$, the number-average molecular weight. This is carried out below.

Molecular wt Range	Mean M_i	x_i	x_iM_i
8,000-16,000	12,000	0.05	600
16,000-24,000	20,000	0.16	3200
24,000-32,000	28,000	0.24	6720
32,000-40,000	36,000	0.28	10,080
40,000-48,000	44,000	0.20	8800
48,000-56,000	52,000	0.07	3640

$$\overline{M}_n = \sum x_i M_i = 33{,}040 \text{ g/mol}$$

(b) From the tabulated data, we are asked to compute $\overline{M}_w$, the weight-average molecular weight.

Molecular wt. Range	Mean M_i	w_i	w_iM_i
8,000-16,000	12,000	0.02	240
16,000-24,000	20,000	0.10	2000
24,000-32,000	28,000	0.20	5600

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32,000-40,000	36,000	0.30	10,800
40,000-48,000	44,000	0.27	11,880
48,000-56,000	52,000	0.11	5720

$$\overline{M}_w = \sum w_i M_i = 36{,}240 \text{ g/mol}$$

(c) Now we are asked to compute the degree of polymerization, which is possible using Equation 14.6. For polypropylene, the repeat unit molecular weight is just

$$m = 3(A_C) + 6(A_H)$$

$$= (3)(12.01 \text{ g/mol}) + (6)(1.008 \text{ g/mol}) = 42.08 \text{ g/mol}$$

And

$$DP = \frac{\overline{M}_n}{m} = \frac{33{,}040 \text{ g/mol}}{42.08 \text{ g/mol}} = 785$$

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14.6 *Molecular weight data for some polymer are tabulated here. Compute (a) the number-average molecular weight, and (b) the weight-average molecular weight. (c) If it is known that this material's degree of polymerization is 710, which one of the polymers listed in Table 14.3 is this polymer? Why?*

Molecular Weight Range g/mol	x_i	w_i
15,000–30,000	*0.04*	*0.01*
30,000–45,000	*0.07*	*0.04*
45,000–60,000	*0.16*	*0.11*
60,000–75,000	*0.26*	*0.24*
75,000–90,000	*0.24*	*0.27*
90,000–105,000	*0.12*	*0.16*
105,000–120,000	*0.08*	*0.12*
120,000–135,000	*0.03*	*0.05*

Solution

(a) From the tabulated data, we are asked to compute $\overline{M}_n$, the number-average molecular weight. This is carried out below.

Molecular wt. Range	Mean M_i	x_i	x_iM_i
15,000-30,000	22,500	0.04	900
30,000-45,000	37,500	0.07	2625
45,000-60,000	52,500	0.16	8400
60,000-75,000	67,500	0.26	17,550
75,000-90,000	82,500	0.24	19,800
90,000-105,000	97,500	0.12	11,700
105,000-120,000	112,500	0.08	9000
120,000-135,000	127,500	0.03	3825

$$\overline{M}_n = \sum x_i M_i = 73{,}800 \text{ g/mol}$$

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(b) From the tabulated data, we are asked to compute $\overline{M}_w$, the weight-average molecular weight. This determination is performed as follows:

Molecular wt. Range	Mean M_i	w_i	w_iM_i
15,000-30,000	22,500	0.01	225
30,000-45,000	37,500	0.04	1500
45,000-60,000	52,500	0.11	5775
60,000-75,000	67,500	0.24	16,200
75,000-90,000	82,500	0.27	22,275
90,000-105,000	97,500	0.16	15,600
105,000-120,000	112,500	0.12	13,500
120,000-135,000	127,500	0.05	6375
			$\overline{M}_w = \sum w_i M_i = 81{,}450$ g/mol

(c) We are now asked if the degree of polymerization is 710, which of the polymers in Table 14.3 is this material? It is necessary to compute *m* in Equation 14.6 as

$$m = \frac{\overline{M}_n}{DP} = \frac{73{,}800 \text{ g/mol}}{710} = 103.94 \text{ g/mol}$$

The repeat unit molecular weights of the polymers listed in Table 14.3 are as follows:

Polyethylene--28.05 g/mol
Poly(vinyl chloride)--62.49 g/mol
Polytetrafluoroethylene--100.02 g/mol
Polypropylene--42.08 g/mol
Polystyrene--104.14 g/mol
Poly(methyl methacrylate)--100.11 g/mol
Phenol-formaldehyde--133.16 g/mol
Nylon 6,6--226.32 g/mol
PET--192.16 g/mol
Polycarbonate--254.27 g/mol

Therefore, polystyrene is the material since its repeat unit molecular weight is closest to that calculated above.

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14.7 *Is it possible to have a poly(methyl methacrylate) homopolymer with the following molecular weight data and a of polymerization of 527? Why or why not?*

Molecular Weight Range (g/mol)	w_i	x_i
8,000–20,000	*0.02*	*0.05*
20,000–32,000	*0.08*	*0.15*
32,000–44,000	*0.17*	*0.21*
44,000–56,000	*0.29*	*0.28*
56,000–68,000	*0.23*	*0.18*
68,000–80,000	*0.16*	*0.10*
80,000–92,000	*0.05*	*0.03*

Solution

This problem asks if it is possible to have a poly(methyl methacrylate) homopolymer with the given molecular weight data and a degree of polymerization of 527. The appropriate data are given below along with a computation of the number-average molecular weight.

Molecular wt. Range	Mean M_i	x_i	$x_i M_i$
8,000-20,000	14,000	0.05	700
20,000-32,000	26,000	0.15	3900
32,000-44,000	38,000	0.21	7980
44,000-56,000	50,000	0.28	14,000
56,000-68,000	62,000	0.18	11,160
68,000-80,000	74,000	0.10	7400
80,000-92,000	86,000	0.03	2580
			$\overline{M}_n = \sum x_i M_i = 47,720$ g/mol

For PMMA, from Table 14.3, each repeat unit has five carbons, eight hydrogens, and two oxygens. Thus,

$$m = 5(A_C) + 8(A_H) + 2(A_O)$$

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$$= (5)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) + (2)(16.00 \text{ g/mol}) = 100.11 \text{ g/mol}$$

Now, we will compute the degree of polymerization using Equation 14.6 as

$$DP = \frac{\overline{M}_n}{m} = \frac{47,720 \text{ g/mol}}{100.11 \text{ g/mol}} = 477$$

Thus, such a homopolymer is *not possible* since the calculated degree of polymerization is 477 (and not 527).

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14.8 *High-density polyethylene may be chlorinated by inducing the random substitution of chlorine atoms for hydrogen.*

(a) Determine the concentration of Cl (in wt%) that must be added if this substitution occurs for 5% of all the original hydrogen atoms.

(b) In what ways does this chlorinated polyethylene differ from poly(vinyl chloride)?

Solution

(a) For chlorinated polyethylene, we are asked to determine the weight percent of chlorine added for 5% Cl substitution of all original hydrogen atoms. Consider 50 carbon atoms; there are 100 possible side-bonding sites. Ninety-five are occupied by hydrogen and five are occupied by Cl. Thus, the mass of these 50 carbon atoms, m_C, is just

$$m_C = 50(A_C) = (50)(12.01 \text{ g/mol}) = 600.5 \text{ g}$$

Likewise, for hydrogen and chlorine,

$$m_H = 95(A_H) = (95)(1.008 \text{ g/mol}) = 95.76 \text{ g}$$

$$m_{Cl} = 5(A_{Cl}) = (5)(35.45 \text{ g/mol}) = 177.25 \text{ g}$$

Thus, the concentration of chlorine, C_{Cl}, is determined using a modified form of Equation 4.3 as

$$C_{Cl} = \frac{m_{Cl}}{m_C + m_H + m_{Cl}} \text{ x } 100$$

$$= \frac{177.25 \text{ g}}{600.5 \text{ g} + 95.76 \text{ g} + 177.25 \text{ g}} \times 100 = 20.3 \text{ wt\%}$$

(b) Chlorinated polyethylene differs from poly(vinyl chloride), in that, for PVC, (1) 25% of the side-bonding sites are substituted with Cl, and (2) the substitution is probably much less random.

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Molecular Shape

14.9 *For a linear polymer molecule, the total chain length L depends on the bond length between chain atoms d, the total number of bonds in the molecule N, and the angle between adjacent backbone chain atoms θ, as follows:*

$$L = Nd \sin\left(\frac{\theta}{2}\right) \qquad (14.11)$$

Furthermore, the average end-to-end distance for a series of polymer molecules r in Figure 14.6 is equal to

$$r = d\sqrt{N} \qquad (14.12)$$

A linear polytetrafluoroethylene has a number-average molecular weight of 500,000 g/mol; compute average values of L and r *for this material.*

Solution

This problem first of all asks for us to calculate, using Equation 14.11, the average total chain length, *L*, for a linear polytetrafluoroethylene polymer having a number-average molecular weight of 500,000 g/mol. It is necessary to calculate the degree of polymerization, *DP*, using Equation 14.6. For polytetrafluoroethylene, from Table 14.3, each repeat unit has two carbons and four flourines. Thus,

$$m = 2(A_C) + 4(A_F)$$

$$= (2)(12.01 \text{ g/mol}) + (4)(19.00 \text{ g/mol}) = 100.02 \text{ g/mol}$$

and

$$DP = \frac{\overline{M}_n}{m} = \frac{500{,}000 \text{ g/mol}}{100.02 \text{ g/mol}} = 5000$$

which is the number of repeat units along an average chain. Since there are two carbon atoms per repeat unit, there are two C—C chain bonds per repeat unit, which means that the total number of chain bonds in the molecule, *N*, is just (2)(5000) = 10,000 bonds. Furthermore, assume that for single carbon-carbon bonds, $d = 0.154$ nm and $\theta = 109°$ (Section 14.4); therefore, from Equation 14.11

$$L = Nd \sin\left(\frac{\theta}{2}\right)$$

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$$= (10,000)(0.154 \text{ nm})\left[\sin\left(\frac{109°}{2}\right)\right] = 1254 \text{ nm}$$

It is now possible to calculate the average chain end-to-end distance, r, using Equation 14.12 as

$$r = d\sqrt{N} = (0.154 \text{ nm})\sqrt{10,000} = 15.4 \text{ nm}$$

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14.10 *Using the definitions for total chain molecule length, L (Equation 14.11) and average chain end-to-end distance r (Equation 14.12), for a linear polyethylene determine:*

(a) the number-average molecular weight for L = 2500 nm;

(b) the number-average molecular weight for r = 20 nm.

Solution

(a) This portion of the problem asks for us to calculate the number-average molecular weight for a linear polyethylene for which L in Equation 14.11 is 2500 nm. It is first necessary to compute the value of N using this equation, where, for the C—C chain bond, $d = 0.154$ nm, and $\theta = 109°$. Thus

$$N = \frac{L}{d \sin\left(\frac{\theta}{2}\right)}$$

$$= \frac{2500 \text{ nm}}{(0.154 \text{ nm}) \sin\left(\frac{109°}{2}\right)} = 19,940$$

Since there are two C—C bonds per polyethylene repeat unit, there is an average of $N/2$ or 19,940/2 = 9970 repeat units per chain, which is also the degree of polymerization, DP. In order to compute the value of $\overline{M}_n$ using Equation 14.6, we must first determine m for polyethylene. Each polyethylene repeat unit consists of two carbon and four hydrogen atoms, thus

$$m = 2(A_C) + 4(A_H)$$

$$= (2)(12.01 \text{ g/mol}) + (4)(1.008 \text{ g/mol}) = 28.05 \text{ g/mol}$$

Therefore

$$\overline{M}_n = (DP)m = (9970)(28.05 \text{ g/mol}) = 280,000 \text{ g/mol}$$

(b) Next, we are to determine the number-average molecular weight for $r = 20$ nm. Solving for N from Equation 14.12 leads to

$$N = \frac{r^2}{d^2} = \frac{(20 \text{ nm})^2}{(0.154 \text{ nm})^2} = 16,900$$

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which is the total number of bonds per average molecule. Since there are two C—C bonds per repeat unit, then $DP = N/2 = 16{,}900/2 = 8450$. Now, from Equation 14.6

$$\overline{M}_n = (DP)m = (8450)(28.05 \text{ g/mol}) = 237{,}000 \text{ g/mol}$$

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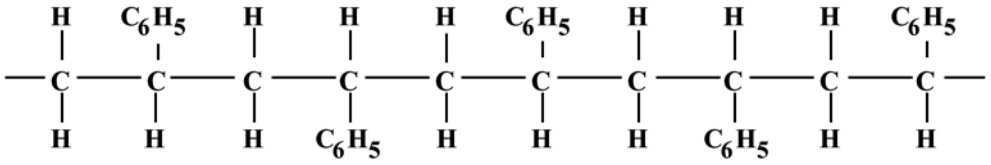
Molecular Configurations

14.11 *Sketch portions of a linear polystyrene molecule that are (a) syndiotactic, (b) atactic, and (c) isotactic. Use two-dimensional schematics per footnote 8 of this chapter.*

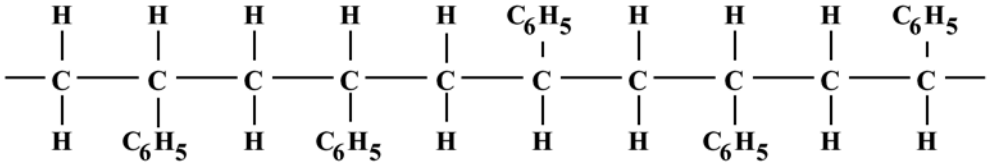
Solution

We are asked to sketch portions of a linear polystyrene molecule for different configurations (using two-dimensional schematic sketches).

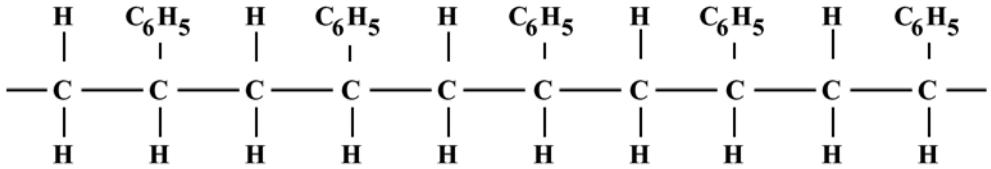
(a) Syndiotactic polystyrene



(b) Atactic polystyrene



(c) Isotactic polystyrene



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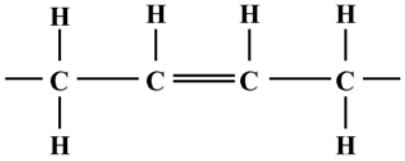
14.12 *Sketch cis and trans structures for (a) butadiene, and (b) chloroprene. Use two-dimensional schematics per footnote 11 of this chapter.*

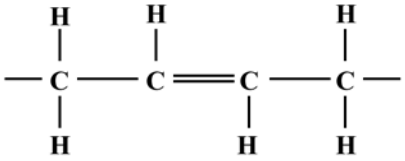
Solution

This problem asks for us to sketch cis and trans structures for butadiene and chloroprene.

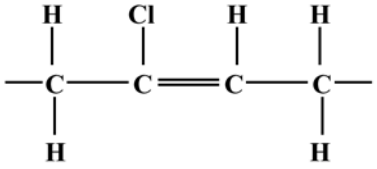
(a) The structure for *cis* polybutadiene (Table 14.5) is



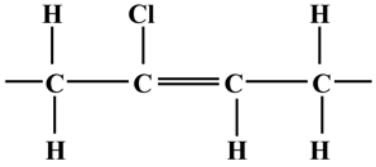
The structure of *trans* butadiene is



(b) The structure of *cis* chloroprene (Table 14.5) is



The structure of *trans* chloroprene is



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Thermoplastic and Thermosetting Polymers

14.13 *Make comparisons of thermoplastic and thermosetting polymers (a) on the basis of mechanical characteristics upon heating, and (b) according to possible molecular structures.*

Solution

(a) Thermoplastic polymers soften when heated and harden when cooled, whereas thermosetting polymers, harden upon heating, while further heating will not lead to softening.

(b) Thermoplastic polymers have linear and branched structures, while for thermosetting polymers, the structures will normally be network or crosslinked.

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14.14 *(a) Is it possible to grind up and reuse phenol-formaldehyde? Why or why not?*

(b) Is it possible to grind up and reuse polypropylene? Why or why not?

Solution

(a) It is *not possible* to grind up and reuse phenol-formaldehyde because it is a network thermoset polymer and, therefore, is not amenable to remolding.

(b) Yes, it is *possible* to grind up and reuse polypropylene since it is a thermoplastic polymer, will soften when reheated, and, thus, may be remolded.

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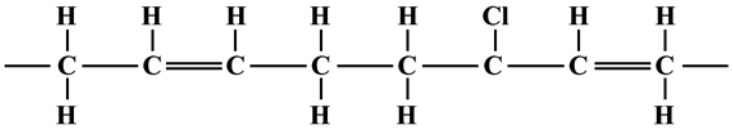
Copolymers

14.15 *Sketch the repeat structure for each of the following alternating copolymers: (a) poly(butadiene-chloroprene), (b) poly(styrene-methyl methacrylate), and (c) poly(acrylonitrile-vinyl chloride).*

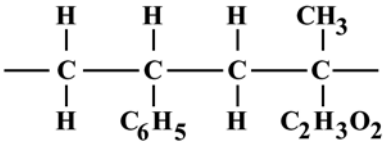
Solution

This problem asks for sketches of the repeat unit structures for several alternating copolymers.

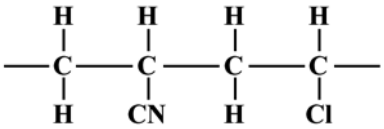
(a) For poly(butadiene-chloroprene)



(b) For poly(styrene-methyl methacrylate)



(c) For poly(acrylonitrile-vinyl chloride)



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14.16 *The number-average molecular weight of a poly(styrene-butadiene) alternating copolymer is 1,350,000 g/mol; determine the average number of styrene and butadiene repeat units per molecule.*

Solution

Since it is an alternating copolymer, the number of both types of repeat units will be the same. Therefore, consider them as a single repeat unit, and determine the number-average degree of polymerization. For the styrene repeat unit, there are eight carbon atoms and eight hydrogen atoms, while the butadiene repeat consists of four carbon atoms and six hydrogen atoms. Therefore, the styrene-butadiene combined repeat unit weight is just

$$m = 12(A_C) + 14(A_H)$$

$$= (12)(12.01 \text{ g/mol}) + (14)(1.008 \text{ g/mol}) = 158.23 \text{ g/mol}$$

From Equation 14.6, the degree of polymerization is just

$$DP = \frac{\overline{M}_n}{m} = \frac{1,350,000 \text{ g/mol}}{158.23 \text{ g/mol}} = 8530$$

Thus, there is an average of 8530 of both repeat unit types per molecule.

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14.17 *Calculate the number-average molecular weight of a random nitrile rubber [poly(acrylonitrile-butadiene) copolymer] in which the fraction of butadiene repeat units is 0.30; assume that this concentration corresponds to a degree of polymerization of 2000.*

Solution

This problem asks for us to calculate the number-average molecular weight of a random nitrile rubber copolymer. For the acrylonitrile repeat unit there are three carbon, one nitrogen, and three hydrogen atoms. Thus, its repeat unit molecular weight is

$$m_{Ac} = 3(A_C) + (A_N) + 3(A_H)$$

$$= (3)(12.01 \text{ g/mol}) + 14.01 \text{ g/mol} + (3)(1.008 \text{ g/mol}) = 53.06 \text{ g/mol}$$

The butadiene repeat unit is composed of four carbon and six hydrogen atoms. Thus, its repeat unit molecular weight is

$$m_{Bu} = 4(A_C) + 6(A_H)$$

$$= (4)(12.01 \text{ g/mol}) + (6)(1.008 \text{ g/mol}) = 54.09 \text{ g/mol}$$

From Equation 14.7, the average repeat unit molecular weight is just

$$\overline{m} = f_{Ac} m_{Ac} + f_{Bu} m_{Bu}$$

$$= (0.70)(53.06 \text{ g/mol}) + (0.30)(54.09 \text{ g/mol}) = 53.37 \text{ g/mol}$$

Since $DP = 2000$ (as stated in the problem), $\overline{M}_n$ may be computed using Equation 14.6 as

$$\overline{M}_n = \overline{m}(DP) = (53.37 \text{ g/mol})(2000) = 106,740 \text{ g/mol}$$

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14.18 *An alternating copolymer is known to have a number-average molecular weight of 250,000 g/mol and a degree of polymerization of 3420. If one of the repeat units is styrene, which of ethylene, propylene, tetrafluoroethylene, and vinyl chloride is the other repeat unit? Why?*

Solution

For an alternating copolymer which has a number-average molecular weight of 250,000 g/mol and a degree of polymerization of 3420, we are to determine one of the repeat unit types if the other is styrene. It is first necessary to calculate $\overline{m}$ using Equation 14.6 as

$$\overline{m} = \frac{\overline{M}_n}{DP} = \frac{250{,}000 \text{ g/mol}}{3420} = 73.10 \text{ g/mol}$$

Since this is an alternating copolymer we know that chain fraction of each repeat unit type is 0.5; that is $f_s = f_x = 0.5$, f_s and f_x being, respectively, the chain fractions of the styrene and unknown repeat units. Also, the repeat unit molecular weight for styrene is

$$m_s = 8(A_C) + 8(A_H)$$

$$= 8(12.01 \text{ g/mol}) + 8(1.008 \text{ g/mol}) = 104.14 \text{ g/mol}$$

Now, using Equation 14.7, it is possible to calculate the repeat unit weight of the unknown repeat unit type, m_x. Thus

$$m_x = \frac{\overline{m} - f_s m_s}{f_x}$$

$$= \frac{73.10 \text{ g/mol} - (0.5)(104.14 \text{ g/mol})}{0.5} = 42.06 \text{ g/mol}$$

Finally, it is necessary to calculate the repeat unit molecular weights for each of the possible other repeat unit types. These are calculated below:

$$m_{\text{ethylene}} = 2(A_C) + 4(A_H) = 2(12.01 \text{ g/mol}) + 4(1.008 \text{ g/mol}) = 28.05 \text{ g/mol}$$
$$m_{\text{propylene}} = 3(A_C) + 6(A_H) = 3(12.01 \text{ g/mol}) + 6(1.008 \text{ g/mol}) = 42.08 \text{ g/mol}$$
$$m_{\text{TFE}} = 2(A_C) + 4(A_F) = 2(12.01 \text{ g/mol}) + 4(19.00 \text{ g/mol}) = 100.02 \text{ g/mol}$$
$$m_{\text{VC}} = 2(A_C) + 3(A_H) + (A_{Cl}) = 2(12.01 \text{ g/mol}) + 3(1.008 \text{ g/mol}) + 35.45 \text{ g/mol} = 62.49 \text{ g/mol}$$

Therefore, propylene is the other repeat unit type since its m value is almost the same as the calculated m_x.

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14.19 *(a) Determine the ratio of butadiene to styrene repeat units in a copolymer having a number-average molecular weight of 350,000 g/mol and degree of polymerization of 4425.*

(b) Which type(s) of copolymer(s) will this copolymer be, considering the following possibilities: random, alternating, graft, and block? Why?

Solution

(a) This portion of the problem asks us to determine the ratio of butadiene to styrene repeat units in a copolymer having a weight-average molecular weight of 350,000 g/mol and a degree of polymerization of 4425. It first becomes necessary to calculate the average repeat unit molecular weight of the copolymer, $\overline{m}$, using Equation 14.6 as

$$\overline{m} = \frac{\overline{M}_n}{DP} = \frac{350{,}000 \text{ g/mol}}{4425} = 79.10 \text{ g/mol}$$

If we designate f_b as the chain fraction of butadiene repeat units, since the copolymer consists of only two repeat unit types, the chain fraction of styrene repeat units f_s is just $1 - f_b$. Now, Equation 14.7 for this copolymer may be written in the form

$$\overline{m} = f_b m_b + f_s m_s = f_b m_b + (1 - f_b) m_s$$

in which m_b and m_s are the repeat unit molecular weights for butadiene and styrene, respectively. These values are calculated as follows:

$$m_b = 4(A_C) + 6(A_H) = 4(12.01 \text{ g/mol}) + 6(1.008 \text{ g/mol}) = 54.09 \text{ g/mol}$$

$$m_s = 8(A_C) + 8(A_H) = 8(12.01 \text{ g/mol}) + 8(1.008 \text{ g/mol}) = 104.14 \text{ g/mol}$$

Solving for f_b in the above expression yields

$$f_b = \frac{\overline{m} - m_s}{m_b - m_s} = \frac{79.10 \text{ g/mol} - 104.14 \text{ g/mol}}{54.09 \text{ g/mol} - 104.14 \text{ g/mol}} = 0.50$$

Furthermore, $f_s = 1 - f_b = 1 - 0.50 = 0.50$; or the ratio is just

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$$\frac{f_b}{f_s} = \frac{0.50}{0.50} = 1.0$$

(b) Of the possible copolymers, the only one for which there is a restriction on the ratio of repeat unit types is alternating; the ratio must be 1:1. Therefore, on the basis of the result in part (a), the possibilities for this copolymer are not only alternating, but also random, graft, and block.

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14.20 *Crosslinked copolymers consisting of 60 wt% ethylene and 40 wt% propylene may have elastic properties similar to those for natural rubber. For a copolymer of this composition, determine the fraction of both repeat unit types.*

Solution

For a copolymer consisting of 60 wt% ethylene and 40 wt% propylene, we are asked to determine the fraction of both repeat unit types.

In 100 g of this material, there are 60 g of ethylene and 40 g of propylene. The ethylene (C_2H_4) molecular weight is

$$m(\text{ethylene}) = 2(A_C) + 4(A_H)$$

$$= (2)(12.01\ \text{g/mol}) + (4)(1.008\ \text{g/mol}) = 28.05\ \text{g/mol}$$

The propylene (C_3H_6) molecular weight is

$$m(\text{propylene}) = 3(A_C) + 6(A_H)$$

$$= (3)(12.01\ \text{g/mol}) + (6)(1.008\ \text{g/mol}) = 42.08\ \text{g/mol}$$

Therefore, in 100 g of this material, there are

$$\frac{60\ \text{g}}{28.05\ \text{g/mol}} = 2.14\ \text{mol of ethylene}$$

and

$$\frac{40\ \text{g}}{42.08\ \text{g/mol}} = 0.95\ \text{mol of propylene}$$

Thus, the fraction of the ethylene repeat unit, f(ethylene), is just

$$f(\text{ethylene}) = \frac{2.14\ \text{mol}}{2.14\ \text{mol} + 0.95\ \text{mol}} = 0.69$$

Likewise,

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$$f(\text{propylene}) = \frac{0.95 \text{ mol}}{2.14 \text{ mol} + 0.95 \text{ mol}} = 0.31$$

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14.21 *A random poly(isobutylene-isoprene) copolymer has a number-average molecular weight of 200,000 g/mol and a degree of polymerization of 3000. Compute the fraction of isobutylene and isoprene repeat units in this copolymer.*

Solution

For a random poly(isobutylene-isoprene) copolymer in which $\overline{M}_n$ = 200,000 g/mol and DP = 3000, we are asked to compute the fractions of isobutylene and isoprene repeat units.

From Table 14.5, the isobutylene repeat unit has four carbon and eight hydrogen atoms. Thus,

$$m_{ib} = (4)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 56.10 \text{ g/mol}$$

Also, from Table 14.5, the isoprene repeat unit has five carbon and eight hydrogen atoms, and

$$m_{ip} = (5)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 68.11 \text{ g/mol}$$

From Equation 14.7

$$\overline{m} = f_{ib}m_{ib} + f_{ip}m_{ip}$$

Now, let $x = f_{ib}$, such that

$$\overline{m} = 56.10x + (68.11)(1 - x)$$

since $f_{ib} + f_{ip} = 1$. Also, from Equation 14.6

$$DP = \frac{\overline{M}_n}{\overline{m}}$$

Or

$$3000 = \frac{200{,}000 \text{ g/mol}}{[56.10x + 68.11(1 - x)] \text{ g/mol}}$$

Solving for x leads to $x = f_{ib} = f$(isobutylene) = 0.12. Also,

$$f\text{(isoprene)} = 1 - x = 1 - 0.12 = 0.88$$

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Polymer Crystallinity

14.22 *Explain briefly why the tendency of a polymer to crystallize decreases with increasing molecular weight.*

Solution

The tendency of a polymer to crystallize decreases with increasing molecular weight because as the chains become longer it is more difficult for all regions along adjacent chains to align so as to produce the ordered atomic array.

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14.23 *For each of the following pairs of polymers, do the following: (1) state whether or not it is possible to determine whether one polymer is more likely to crystallize than the other; (2) if it is possible, note which is the more likely and then cite reason(s) for your choice; and (3) if it is not possible to decide, then state why.*

(a) Linear and syndiotactic poly(vinyl chloride); linear and isotactic polystyrene.

(b) Network phenol-formaldehyde; linear and heavily crosslinked cis-isoprene.

(c) Linear polyethylene; lightly branched isotactic polypropylene.

(d) Alternating poly(styrene-ethylene) copolymer; random poly(vinyl chloride-tetrafluoroethylene) copolymer.

Solution

(a) Yes, for these two polymers it is possible to decide. The linear and syndiotactic poly(vinyl chloride) is more likely to crystallize; the phenyl side-group for polystyrene is bulkier than the Cl side-group for poly(vinyl chloride). Syndiotactic and isotactic isomers are equally likely to crystallize.

(b) No, it is not possible to decide for these two polymers. Both heavily crosslinked and network polymers are not likely to crystallize.

(c) Yes, it is possible to decide for these two polymers. The linear polyethylene is more likely to crystallize. The repeat unit structure for polypropylene is chemically more complicated than is the repeat unit structure for polyethylene. Furthermore, branched structures are less likely to crystallize than are linear structures.

(d) Yes, it is possible to decide for these two copolymers. The alternating poly(styrene-ethylene) copolymer is more likely to crystallize. Alternating copolymers crystallize more easily than do random copolymers.

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14.24 *The density of totally crystalline polypropylene at room temperature is 0.946 g/cm^3. Also, at room temperature the unit cell for this material is monoclinic with lattice parameters*

$a = 0.666$ nm $\qquad \alpha = 90°$

$b = 2.078$ nm $\qquad \beta = 99.62°$

$c = 0.650$ nm $\qquad \gamma = 90°$

If the volume of a monoclinic unit cell, V_{mono}, is a function of these lattice parameters as

$$V_{mono} = abc \sin \beta$$

determine the number of repeat units per unit cell.

Solution

For this problem we are given the density of polypropylene (0.946 g/cm^3), an expression for the volume of its unit cell, and the lattice parameters, and are asked to determine the number of repeat units per unit cell. This computation necessitates the use of Equation 3.5, in which we solve for n. Before this can be carried out we must first calculate V_C, the unit cell volume, and A the repeat unit molecular weight. For V_C

$$V_C = abc \sin \beta$$

$$= (0.666 \text{ nm})(2.078 \text{ nm})(0.650 \text{ nm}) \sin (99.62°)$$

$$= 0.8869 \text{ nm}^3 = 8.869 \times 10^{-22} \text{ cm}^3$$

The repeat unit for polypropylene is shown in Table 14.3, from which the value of A may be determined as follows:

$$A = 3(A_C) + 6(A_H)$$

$$= 3(12.01 \text{ g/mol}) + 6(1.008 \text{ g/mol})$$

$$= 42.08 \text{ g/mol}$$

Finally, solving for n from Equation 3.5 leads to

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$$n = \frac{\rho V_C N_A}{A}$$

$$= \frac{(0.946 \text{ g/cm}^3)(8.869 \times 10^{-22} \text{ cm}^3\text{/unit cell})(6.022 \times 10^{23} \text{ repeat units/mol})}{42.08 \text{ g/mol}}$$

$$= 12.0 \text{ repeat unit/unit cell}$$

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14.25 *The density and associated percent crystallinity for two polytetrafluoroethylene materials are as follows:*

ρ (g/cm^3)	crystallinity (%)
2.144	51.3
2.215	74.2

(a) Compute the densities of totally crystalline and totally amorphous polytetrafluoroethylene.

(b) Determine the percent crystallinity of a specimen having a density of 2.26 g/cm^3.

Solution

(a) We are asked to compute the densities of totally crystalline and totally amorphous polytetrafluoroethylene (ρ_c and ρ_a from Equation 14.8). From Equation 14.8 let $C = \frac{\%\ \text{crystallinity}}{100}$, such that

$$C = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)}$$

Rearrangement of this expression leads to

$$\rho_c(C\rho_s - \rho_s) + \rho_c\rho_a - C\rho_s\rho_a = 0$$

in which ρ_c and ρ_a are the variables for which solutions are to be found. Since two values of ρ_s and C are specified in the problem statement, two equations may be constructed as follows:

$$\rho_c(C_1\rho_{s1} - \rho_{s1}) + \rho_c\rho_a - C_1\rho_{s1}\rho_a = 0$$

$$\rho_c(C_2\rho_{s2} - \rho_{s2}) + \rho_c\rho_a - C_2\rho_{s2}\rho_a = 0$$

In which ρ_{s1} = 2.144 g/cm^3, ρ_{s2} = 2.215 g/cm^3, C_1 = 0.513, and C_2 = 0.742. Solving the above two equations for ρ_a and ρ_c leads to

$$\rho_a = \frac{\rho_{s1}\rho_{s2}(C_1 - C_2)}{C_1\rho_{s1} - C_2\rho_{s2}}$$

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$$= \frac{(2.144\ \text{g/cm}^3)(2.215\ \text{g/cm}^3)(0.513\ -\ 0.742)}{(0.513)(2.144\ \text{g/cm}^3)\ -\ (0.742)(2.215\ \text{g/cm}^3)} = 2.000\ \text{g/cm}^3$$

And

$$\rho_c = \frac{\rho_{s1}\rho_{s2}(C_2\ -\ C_1)}{\rho_{s2}(C_2\ -\ 1)\ -\ \rho_{s1}(C_1\ -\ 1)}$$

$$= \frac{(2.144\ \text{g/cm}^3)(2.215\ \text{g/cm}^3)(0.742\ -\ 0.513)}{(2.215\ \text{g/cm}^3)(0.742\ -\ 1)\ -\ (2.144\ \text{g/cm}^3)(0.513\ -\ 1)} = 2.301\ \text{g/cm}^3$$

(b) Now we are to determine the % crystallinity for $\rho_s = 2.26\ \text{g/cm}^3$. Again, using Equation 14.8

$$\%\ \text{crystallinity} = \frac{\rho_c(\rho_s\ -\ \rho_a)}{\rho_s(\rho_c\ -\ \rho_a)} \times 100$$

$$= \frac{(2.301\ \text{g/cm}^3)(2.260\ \text{g/cm}^3\ -\ 2.000\ \text{g/cm}^3)}{(2.260\ \text{g/cm}^3)(2.301\ \text{g/cm}^3\ -\ 2.000\ \text{g/cm}^3)} \times 100$$

$$= 87.9\%$$

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14.26 *The density and associated percent crystallinity for two nylon 6,6 materials are as follows:*

ρ (g/cm^3)	crystallinity (%)
1.188	67.3
1.152	43.7

(a) Compute the densities of totally crystalline and totally amorphous nylon 6,6.

(b) Determine the density of a specimen having 55.4% crystallinity.

Solution

(a) We are asked to compute the densities of totally crystalline and totally amorphous nylon 6,6 (ρ_c and ρ_a from Equation 14.8). From Equation 14.8 let $C = \frac{\%\ \text{crystallinity}}{100}$, such that

$$C = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)}$$

Rearrangement of this expression leads to

$$\rho_c(C\rho_s - \rho_s) + \rho_c\rho_a - C\rho_s\rho_a = 0$$

in which ρ_c and ρ_a are the variables for which solutions are to be found. Since two values of ρ_s and C are specified in the problem, two equations may be constructed as follows:

$$\rho_c(C_1\rho_{s1} - \rho_{s1}) + \rho_c\rho_a - C_1\rho_{s1}\rho_a = 0$$

$$\rho_c(C_2\rho_{s2} - \rho_{s2}) + \rho_c\rho_a - C_2\rho_{s2}\rho_a = 0$$

In which $\rho_{s1} = 1.188$ g/cm^3, $\rho_{s2} = 1.152$ g/cm^3, $C_1 = 0.673$, and $C_2 = 0.437$. Solving the above two equations for ρ_a and ρ_c leads to

$$\rho_a = \frac{\rho_{s1}\rho_{s2}(C_1 - C_2)}{C_1\rho_{s1} - C_2\rho_{s2}}$$

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$$= \frac{(1.188\ \text{g/cm}^3)(1.152\ \text{g/cm}^3)(0.673-0.437)}{(0.673)(1.188\ \text{g/cm}^3)-(0.437)(1.152\ \text{g/cm}^3)} = 1.091\ \text{g/cm}^3$$

And

$$\rho_c = \frac{\rho_{s1}\rho_{s2}(C_2 - C_1)}{\rho_{s2}(C_2 - 1) - \rho_{s1}(C_1 - 1)}$$

$$= \frac{(1.188\ \text{g/cm}^3)(1.152\ \text{g/cm}^3)(0.437-0.673)}{(1.152\ \text{g/cm}^3)(0.437-1) - (1.188\ \text{g/cm}^3)(0.673-1)} = 1.242\ \text{g/cm}^3$$

(b) Now we are asked to determine the density of a specimen having 55.4% crystallinity. Solving for ρ_s from Equation 14.8 and substitution for ρ_a and ρ_c which were computed in part (a) yields

$$\rho_s = \frac{-\rho_c\rho_a}{C(\rho_c-\rho_a)-\rho_c}$$

$$= \frac{-(1.242\ \text{g/cm}^3)(1.091\ \text{g/cm}^3)}{(0.554)(1.242\ \text{g/cm}^3 - 1.091\ \text{g/cm}^3) - 1.242\ \text{g/cm}^3}$$

$$= 1.170\ \text{g/cm}^3$$

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Diffusion in Polymeric Materials

14.27 *Consider the diffusion of water vapor through a polypropylene (PP) sheet 2 mm thick. The pressures of H_2O at the two faces are 1 kPa and 10 kPa, which are maintained constant. Assuming conditions of steady state, what is the diffusion flux [in [(cm^3 STP)/cm^2-s] at 298 K?*

Solution

This is a permeability problem in which we are asked to compute the diffusion flux of water vapor through a 2-mm thick sheet of polypropylene. In order to solve this problem it is necessary to employ Equation 14.9. The permeability coefficient of H_2O through PP is given in Table 14.6 as 38×10^{-13} (cm^3 STP)-cm/cm^2-s-Pa. Thus, from Equation 14.9

$$J = P_M \frac{\Delta P}{\Delta x} = P_M \frac{P_2 - P_1}{\Delta x}$$

and taking P_1 = 1 kPa (1,000 Pa) and P_2 = 10 kPa (10,000 Pa) we get

$$= \left[38 \times 10^{-13} \frac{(\text{cm}^3 \text{ STP})(\text{cm})}{\text{cm}^2 \text{ - s - Pa}} \right] \left(\frac{10{,}000 \text{ Pa} - 1{,}000 \text{ Pa}}{0.2 \text{ cm}} \right)$$

$$= 1.71 \times 10^{-7} \frac{(\text{cm}^3 \text{ STP})}{\text{cm}^2 \text{ - s}}$$

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14.28 *Argon diffuses through a high density polyethylene (HDPE) sheet 40 mm thick at a rate of* 4.0×10^{-7} *(cm*^{3} *STP)/cm*^{2}*-s at 325 K. The pressures of argon at the two faces are 5000 kPa and 1500 kPa, which are maintained constant. Assuming conditions of steady state, what is the permeability coefficient at 325 K?*

Solution

This problem asks us to compute the permeability coefficient for argon through high density polyethylene at 325 K given a steady-state permeability situation. It is necessary for us to Equation 14.9 in order to solve this problem. Rearranging this expression and solving for the permeability coefficient gives

$$P_M = \frac{J \Delta x}{\Delta P} = \frac{J \Delta x}{P_2 - P_1}$$

Taking P_1 = 1500 kPa (1,500,000 Pa) and P_2 = 5000 kPa (5,000,000 Pa), the permeability coefficient of Ar through HDPE is equal to

$$P_M = \frac{\left[4.0 \times 10^{-7} \frac{(\text{cm}^3 \text{ STP})}{\text{cm}^2 \text{ - s}}\right](4 \text{ cm})}{(5{,}000{,}000 \text{ Pa} - 1{,}500{,}000 \text{ Pa})}$$

$$= 4.57 \times 10^{-13} \frac{(\text{cm}^3 \text{ STP})(\text{cm})}{\text{cm}^2 \text{ - s - Pa}}$$

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14.29 *The permeability coefficient of a type of small gas molecule in a polymer is dependent on absolute temperature according to the following equation:*

$$P_M = P_{M_0} \exp\left(-\frac{Q_p}{RT}\right)$$

where P_{M_0} *and* Q_p *are constants for a given gas-polymer pair. Consider the diffusion of hydrogen through a poly(dimethyl siloxane) (PDMSO) sheet 20 mm thick. The hydrogen pressures at the two faces are 10 kPa and 1 kPa, which are maintained constant. Compute the diffusion flux [in* $(cm^3\ STP)/cm^2$ *–s] at 350 K. For this diffusion system*

$P_{M_0} = 1.45 \times 10^{-8}\ (cm^3\ STP)(cm)/cm^2 - s - Pa$

$Q_p = 13.7\ kJ/mol$

Also, assume a condition of steady state diffusion

Solution

This problem asks that we compute the diffusion flux at 350 K for hydrogen in poly(dimethyl siloxane) (PDMSO). It is first necessary to compute the value of the permeability coefficient at 350 K. The temperature dependence of P_M is given in the problem statement, as follows:

$$P_M = P_{M_0} \exp\left(-\frac{Q_p}{RT}\right)$$

And, incorporating values provided for the constants P_{M_0} and Q_p, we get

$$P_M = \left[1.45 \times 10^{-8}\ \frac{(\text{cm}^3\ \text{STP})(\text{cm})}{\text{cm}^2 - \text{s} - \text{Pa}}\right] \exp\left[-\frac{13{,}700\ \text{J/mol}}{(8.31\ \text{J/mol-K})(350\ \text{K})}\right]$$

$$= 1.31 \times 10^{-10}\ \frac{(\text{cm}^3\ \text{STP})(\text{cm})}{\text{cm}^2 - \text{s} - \text{Pa}}$$

And, using Equation 14.9, the diffusion flux is equal to

$$J = P_M \frac{\Delta P}{\Delta x} = P_M \frac{P_2 - P_1}{\Delta x}$$

$$= 1.31 \times 10^{-10} \frac{(\text{cm}^3\ \text{STP})(\text{cm})}{\text{cm}^2 - \text{s} - \text{Pa}} \left(\frac{10{,}000\ \text{Pa} - 1{,}000\ \text{Pa}}{2.0\ \text{cm}}\right)$$

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$$= 5.90 \times 10^{-7} \frac{(\text{cm}^3 \text{ STP})}{\text{cm}^2 \text{ - s}}$$

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CHAPTER 15

CHARACTERISTICS, APPLICATIONS, AND PROCESSING OF POLYMERS

PROBLEM SOLUTIONS

Stress-Strain Behavior

15.1 *From the stress–strain data for poly(methyl methacrylate) shown in Figure 15.3, determine the modulus of elasticity and tensile strength at room temperature [20°C (68°F)], and compare these values with those given in Table 15.1.*

Solution

From Figure 15.3, the elastic modulus is the slope in the elastic linear region of the 20°C curve, which is

$$E = \frac{\Delta(\text{stress})}{\Delta(\text{strain})} = \frac{30\ \text{MPa} - 0\ \text{MPa}}{9 \times 10^{-3} - 0} = 3.3\ \text{GPa} \quad (483{,}000\ \text{psi})$$

The value range cited in Table 15.1 is 2.24 to 3.24 GPa (325,000 to 470,000 psi). Thus, the plotted value is a little on the high side.

The tensile strength corresponds to the stress at which the curve ends, which is 52 MPa (7500 psi). This value lies within the range cited in Table 15.1—48.3 to 72.4 MPa (7000 to 10,500 psi).

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15.2 *Compute the elastic moduli for the following polymers, whose stress-strain behaviors may be observed in the "Tensile Tests" module of Virtual Materials Science and Engineering (VMSE): (a) high-density polyethylene, (b) nylon, and (c) phenol-formaldehyde (bakelite). How do these values compare with those presented in Table 15.1 for the same polymers?*

Solution

The elastic modulus is the slope in the linear elastic region (Equation 6.10) as

$$E = \frac{\Delta\sigma}{\Delta\varepsilon} = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1}$$

Since all the stress-strain curves pass through the origin, we make take $\sigma_1 = 0$ and $\varepsilon_1 = 0$. Determinations of σ_2 and ε_2 are possible by moving the cursor to some arbitrary point in the linear region of the curve and then reading corresponding values in the "Stress" and "Strain" windows that are located below the plot.

(a) For high-density polyethylene, we selected $\sigma_2 = 6.0$ MPa with its corresponding $\varepsilon_2 = 0.0152$. Therefore,

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{6.0\ \text{MPa} - 0\ \text{MPa}}{0.0152 - 0} = 395\ \text{MPa} = 0.395\ \text{GPa}$$

The elastic modulus (average) for high-density polyethylene given in Table 15.1 is 1.08 GPa, which is significantly higher than this value.

(b) For nylon, we selected $\sigma_2 = 24.3$ MPa with its corresponding $\varepsilon_2 = 0.0085$. Therefore,

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{24.3\ \text{MPa} - 0\ \text{MPa}}{0.0085 - 0} = 2860\ \text{MPa} = 2.86\ \text{GPa}$$

The elastic modulus range for nylon 6,6 given in Table 15.1 is 1.58 GPa to 3.80 GPa; therefore, the value for the *VMSE* nylon lies within this range.

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(c) For phenol-formaldehyde (bakelite), we selected $\sigma_2 = 33.0$ MPa with its corresponding $\varepsilon_2 = 0.0068$. Therefore,

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{33.0 \text{ MPa} - 0 \text{ MPa}}{0.0068 - 0} = 4850 \text{ MPa} = 4.85 \text{ GPa}$$

The elastic modulus range for the phenol-formaldehyde given in Table 15.1 is 2.76 GPa to 4.83 GPa; therefore, this value for the *VMSE* phenol-formaldehyde lies just above the maximum value for this range.

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15.3 *For the nylon polymer, whose stress strain behavior may be observed in the "Tensile Tests" module of Virtual Materials Science and Engineering (VMSE), determine the following:*

(a) the yield strength, and

(b) the approximate ductility, in percent elongation.

How do these values compare with those for the nylon material presented in Table 15.1?

Solution

(a) The yield strength corresponds to the first maximum (just beyond the initial linear-elastic region) of the stress-strain curve. This reading in the stress window located below the plot as the curser point is dragged along the stress-strain curve is 84 MPa.

(b) The approximate percent elongation corresponds to the strain at fracture multiplied by 100 (i.e., 44.5%) minus the maximum elastic strain (i.e., value of strain at which the linearity of the curve ends multiplied by 100—in this case about 4%); this gives a value of about 40%EL.

For nylon 6,6, the range of values of yield strength presented in Table 15.1 is 44.8 MPa to 82.8 MPa; therefore, the value for the *VMSE* nylon lies slightly above the upper value. The ductility range for nylon 6,6 is 15%EL to 300%EL; therefore, our value (40%EL) lies within this range.

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15.4 *For the phenol-formaldehyde (Bakelite) polymer, whose stress strain behavior may be observed in the "Tensile Tests" module of Virtual Materials Science and Engineering (VMSE), determine the following:*

(a) the tensile strength, and

(b) the approximate ductility, in percent elongation.

How do these values compare with those for the phenol-formaldehyde material presented in Table 15.1?

Solution

(a) The tensile strength corresponds to the stress at which fracture occurs. This reading in the stress window located below the plot as the curser point is dragged along the stress-strain curve is 52 MPa.

(b) The approximate percent elongation corresponds to the strain at fracture multiplied by 100 (i.e., 1.29%) minus the maximum elastic strain (i.e., value of strain at which the linearity of the curve ends multiplied by 100—in this case about 1%); this gives a value of about 0.3%EL.

For phenol-formaldehyde, the range of values of tensile strength presented in Table 15.1 is 34.5 MPa to 62.1 MPa; therefore, the value for the *VMSE* material (52 MPa) lies within this range. The ductility range for phenol-formaldehyde is 1.5%EL to 2.0%EL; therefore, our value (0.3%EL) lies below the lower limit.

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Viscoelastic Deformation

15.5 *In your own words, briefly describe the phenomenon of viscoelasticity.*

The explanation of viscoelasticity is given in Section 15.4.

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15.6 *For some viscoelastic polymers that are subjected to stress relaxation tests, the stress decays with time according to*

$$\sigma(t) = \sigma(0) \exp\left(-\frac{t}{\tau}\right) \qquad (15.10)$$

where σ(t) and σ(0) represent the time-dependent and initial (i.e., time = 0) stresses, respectively, and t and τ denote elapsed time and the relaxation time; τ is a time-independent constant characteristic of the material. A specimen of some viscoelastic polymer the stress relaxation of which obeys Equation 15.10 was suddenly pulled in tension to a measured strain of 0.6; the stress necessary to maintain this constant strain was measured as a function of time. Determine $E_r(10)$ for this material if the initial stress level was 2.76 MPa (400 psi), which dropped to 1.72 MPa (250 psi) after 60 s.

Solution

This problem asks for a determination of the relaxation modulus of a viscoelastic material, which behavior is according to Equation 15.10--i.e.,

$$\sigma(t) = \sigma(0) \exp\left(-\frac{t}{\tau}\right)$$

We want to determine σ(10), but it is first necessary to compute τ from the data provided in the problem statement. Thus, solving for τ from the above expression,

$$\tau = \frac{-t}{\ln\left[\frac{\sigma(t)}{\sigma(0)}\right]} = \frac{-60 \text{ s}}{\ln\left[\frac{1.72 \text{ MPa}}{2.76 \text{ MPa}}\right]} = 127 \text{ s}$$

Therefore,

$$\sigma(10) = (2.76 \text{ MPa}) \exp\left(-\frac{10 \text{ s}}{127 \text{ s}}\right) = 2.55 \text{ MPa}$$

Now, using Equation 15.1

$$E_r(10) = \frac{\sigma(10)}{\varepsilon_0} = \frac{2.55 \text{ MPa}}{0.6} = 4.25 \text{ MPa} \quad (616 \text{ psi})$$

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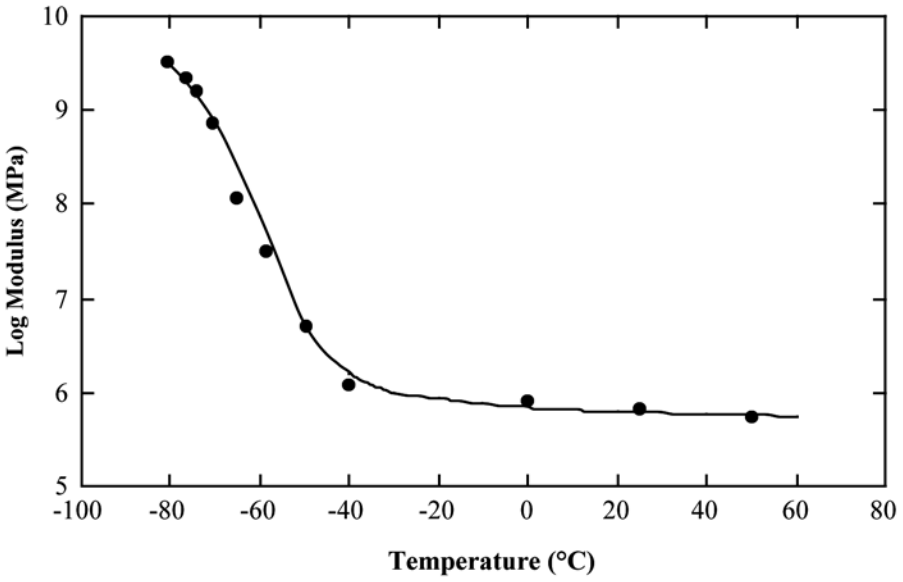
15.7 *In Figure 15.28, the logarithm of $E_r(t)$ versus the logarithm of time is plotted for polyisobutylene at a variety of temperatures. Make a plot of $E_r(10)$ versus temperature and then estimate its T_g.*

Solution

Below is plotted the logarithm of $E_r(10)$ versus temperature.



The glass-transition temperature is that temperature corresponding to the abrupt decrease in log $E_r(10)$, which for this polyisobutylene material is about -60°C.

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15.8 *On the basis of the curves in Figure 15.5, sketch schematic strain–time plots for the following polystyrene materials at the specified temperatures:*

(a) Amorphous at 120°C

(b) Crosslinked at 150°C

(c) Crystalline at 230°C

(d) Crosslinked at 50°C

Solution

(a) Amorphous polystyrene at 120°C behaves a rubbery material (Figure 15.8, curve *C*); therefore, the strain-time behavior would be as Figure 15.5*c*.

(b) Crosslinked polystyrene at 150°C behaves as a viscoelastic material (Figure 15.8, curve *B*); therefore, the strain-time behavior will be as Figure 15.5*c*.

(c) Crystalline polystyrene at 230°C behaves as a viscous liquid (Figure 15.8, curve *A*); therefore, the strain-time behavior will be as Figure 15.5*d*.

(d) Crosslinked polystyrene at 50°C behaves in a glassy manner (Figure 15.8, curve *B*); therefore, the strain-time behavior will be as Figure 15.5*b*.

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15.9 *(a) Contrast the manner in which stress relaxation and viscoelastic creep tests are conducted.*

(b) For each of these tests, cite the experimental parameter of interest and how it is determined.

Solution

(a) Stress relaxation tests are conducted by rapidly straining the material elastically in tension, holding the strain level constant, and then measuring the stress as a function of time. For viscoelastic creep tests, a stress (usually tensile) is applied instantaneously and maintained constant while strain is measured as a function of time.

(b) The experimental parameters of interest from the stress relaxation and viscoelastic creep tests are the relaxation modulus and creep modulus (or creep compliance), respectively. The relaxation modulus is the ratio of stress measured after 10 s and strain (Equation 15.1); creep modulus is the ratio of stress and strain taken at a specific time (Equation 15.2).

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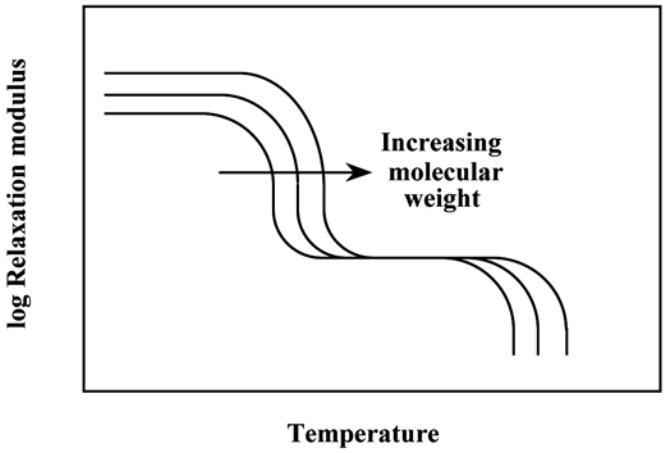
15.10 *Make two schematic plots of the logarithm of relaxation modulus versus temperature for an amorphous polymer (curve C in Figure 15.8).*

(a) On one of these plots demonstrate how the behavior changes with increasing molecular weight.

(b) On the other plot, indicate the change in behavior with increasing crosslinking.

Solution

(a) This portion of the problem calls for a plot of log $E_r(10)$ versus temperature demonstrating how the behavior changes with increased molecular weight. Such a plot is given below. Increasing molecular weight increases both glass-transition and melting temperatures.



(b) We are now called upon to make a plot of log $E_r(10)$ versus temperature demonstrating how the behavior changes with increased crosslinking. Such a plot is given below. Increasing the degree of crosslinking will increase the modulus in both glassy and rubbery regions.

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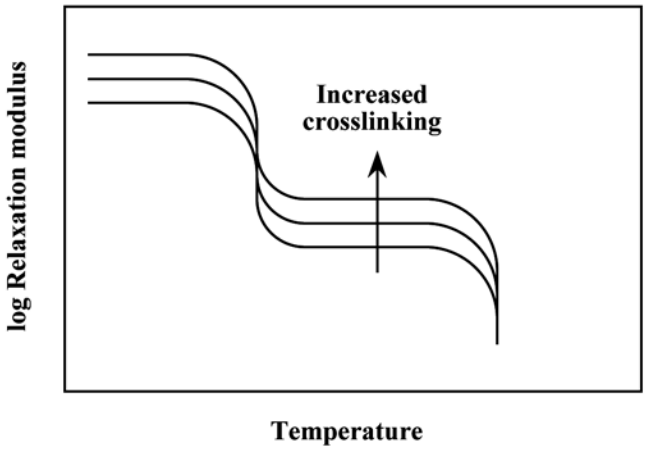

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Fracture of Polymers
Miscellaneous Mechanical Considerations

15.11 *For thermoplastic polymers, cite five factors that favor brittle fracture.*

Solution

For thermoplastic polymers, five factors that favor brittle fracture are as follows: (1) a reduction in temperature, (2) an increase in strain rate, (3) the presence of a sharp notch, (4) increased specimen thickness, and (5) modifications of the polymer structure.

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15.12 *(a) Compare the fatigue limits for polystyrene (Figure 15.11) and the cast iron for which fatigue data are given in Problem 8.20.*

(b) Compare the fatigue strengths at 10^6 cycles for poly(ethylene terephthalate) (PET, Figure 15.11) and red brass (Figure 8.34).

Solution

(a) The fatigue limits for polystyrene and the cast iron are 10.5 MPa (1500 psi) and 193 MPa (28,000 psi), respectively.

(b) At 10^6 cycles, the fatigue strengths of PET and red brass are 15 MPa (2175 psi) and 115 MPa (16,700 psi), respectively.

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Deformation of Semicrystalline Polymers

15.13 *In your own words, describe the mechanisms by which semicrystalline polymers (a) elastically deform and (b) plastically deform, and (c) by which elastomers elastically deform.*

(a) and (b) The mechanisms by which semicrystalline polymers elastically and plastically deform are described in Section 15.7.

(c) The explanation of the mechanism by which elastomers elastically deform is provided in Section 15.9.

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Factors That Influence the Mechanical Properties of Semicrystalline Polymers

Deformation of Elastomers

15.14 *Briefly explain how each of the following influences the tensile modulus of a semicrystalline polymer and why:*

(a) Molecular weight

(b) Degree of crystallinity

(c) Deformation by drawing

(d) Annealing of an undeformed material

(f) Annealing of a drawn material

Solution

(a) The tensile modulus is not directly influenced by a polymer's molecular weight.

(b) Tensile modulus increases with increasing degree of crystallinity for semicrystalline polymers. This is due to enhanced secondary interchain bonding which results from adjacent aligned chain segments as percent crystallinity increases. This enhanced interchain bonding inhibits relative interchain motion.

(c) Deformation by drawing also increases the tensile modulus. The reason for this is that drawing produces a highly oriented molecular structure, and a relatively high degree of interchain secondary bonding.

(d) When an undeformed semicrystalline polymer is annealed below its melting temperature, the tensile modulus increases.

(e) A drawn semicrystalline polymer that is annealed experiences a decrease in tensile modulus as a result of a reduction in chain-induced crystallinity, and a reduction in interchain bonding forces.

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15.15 *Briefly explain how each of the following influences the tensile or yield strength of a semicrystalline polymer and why:*

(a) Molecular weight

(b) Degree of crystallinity

(c) Deformation by drawing

(d) Annealing of an undeformed material

Solution

(a) The tensile strength of a semicrystalline polymer increases with increasing molecular weight. This effect is explained by increased chain entanglements at higher molecular weights.

(b) Increasing the degree of crystallinity of a semicrystalline polymer leads to an enhancement of the tensile strength. Again, this is due to enhanced interchain bonding and forces; in response to applied stresses, interchain motions are thus inhibited.

(c) Deformation by drawing increases the tensile strength of a semicrystalline polymer. This effect is due to the highly oriented chain structure that is produced by drawing, which gives rise to higher interchain secondary bonding forces.

(d) Annealing an undeformed semicrystalline polymer produces an increase in its tensile strength.

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15.16 *Normal butane and isobutane have boiling temperatures of –0.5 and –12.3°C (31.1 and 9.9°F), respectively. Briefly explain this behavior on the basis of their molecular structures, as presented in Section 14.2.*

Solution

Normal butane has a higher melting temperature as a result of its molecular structure (Section 14.2). There is more of an opportunity for van der Waals bonds to form between two molecules in close proximity to one another than for isobutane because of the linear nature of each normal butane molecule.

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15.17 *The tensile strength and number-average molecular weight for two poly(methyl methacrylate) materials are as follows:*

***Tensile Strength* (*MPa*)**	***Number-Average Molecular Weight* (*g/mol*)**
107	*40,000*
170	*60,000*

Estimate the tensile strength at a number-average molecular weight of 30,000 g/mol.

Solution

This problem gives us the tensile strengths and associated number-average molecular weights for two poly(methyl methacrylate) materials and then asks that we estimate the tensile strength for $\overline{M}_n$ = 30,000 g/mol. Equation 15.3 cites the dependence of the tensile strength on $\overline{M}_n$. Thus, using the data provided in the problem statement, we may set up two simultaneous equations from which it is possible to solve for the two constants TS_∞ and A. These equations are as follows:

$$107 \text{ MPa} = TS_\infty - \frac{A}{40{,}000 \text{ g/mol}}$$

$$170 \text{ MPa} = TS_\infty - \frac{A}{60{,}000 \text{ g/mol}}$$

Thus, the values of the two constants are: TS_∞ = 296 MPa and $A = 7.56 \times 10^6$ MPa-g/mol. Substituting these values into Equation 15.3 for $\overline{M}_n$ = 30,000 g/mol leads to

$$TS = TS_\infty - \frac{A}{30{,}000 \text{ g/mol}}$$

$$= 296 \text{ MPa} - \frac{7.56 \times 10^6 \text{ MPa-g/mol}}{30{,}000 \text{ g/mol}}$$

$$= 44 \text{ MPa}$$

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15.18 *The tensile strength and number-average molecular weight for two polyethylene materials are as follows:*

***Tensile Strength* (*MPa*)**	***Number-Average Molecular Weight* (*g/mol*)**
85	*12,700*
150	*28,500*

Estimate the number-average molecular weight that is required to give a tensile strength of 195 MPa.

Solution

This problem gives us the tensile strengths and associated number-average molecular weights for two polyethylene materials and then asks that we estimate the $\overline{M}_n$ that is required for a tensile strength of 195 MPa. Equation 15.3 cites the dependence of the tensile strength on $\overline{M}_n$. Thus, using the data provided in the problem statement, we may set up two simultaneous equations from which it is possible to solve for the two constants TS_∞ and A. These equations are as follows:

$$85 \text{ MPa} = TS_\infty - \frac{A}{12,700 \text{ g/mol}}$$

$$150 \text{ MPa} = TS_\infty - \frac{A}{28,500 \text{ g/mol}}$$

Thus, the values of the two constants are: $TS_\infty = 202$ MPa and $A = 1.489 \times 10^6$ MPa-g/mol. Solving for $\overline{M}_n$ in Equation 15.3 and substituting $TS = 195$ MPa as well as the above values for TS_∞ and A leads to

$$\overline{M}_n = \frac{A}{TS_\infty - TS}$$

$$= \frac{1.489 \times 10^6 \text{ MPa-g/mol}}{202 \text{ MPa} - 195 \text{ MPa}} = 213,000 \text{ g/mol}$$

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15.19 *For each of the following pairs of polymers, do the following: (1) state whether or not it is possible to decide whether one polymer has a higher tensile modulus than the other; (2) if this is possible, note which has the higher tensile modulus and then cite the reason(s) for your choice; and (3) if it is not possible to decide, then state why.*

(a) Random acrylonitrile-butadiene copolymer with 10% of possible sites crosslinked; alternating acrylonitrile-butadiene copolymer with 5% of possible sites crosslinked

(b) Branched and syndiotactic polypropylene with a degree of polymerization of 5000; linear and isotactic polypropylene with a degree of polymerization of 3000

(c) Branched polyethylene with a number-average molecular weight of 250,000 g/mol; linear and isotactic poly(vinyl chloride) with a number-average molecular weight of 200,000 g/mol

Solution

For each of four pairs of polymers, we are to do the following: (1) determine whether or not it is possible to decide which has the higher tensile modulus; (2) if so, note which has the higher tensile modulus and then state the reasons for this choice; and (3) if it is not possible to decide, then state why.

(a) No, it is not possible. The random acrylonitrile-butadiene copolymer will tend to a lower degree of crystallinity than the alternating acrylonitrile-butadiene copolymer inasmuch as random copolymers don't normally crystallize. On this basis only, the alternating material would have a higher modulus inasmuch as tensile modulus increases with degree of crystallinity. On the other hand, the random copolymer has a higher degree of crosslinking (10% versus 5% for the alternating copolymer), and, on this basis only would have the higher tensile modulus—an increase in crosslinking leads to an increase in E. Thus, this determination is not possible; with regard to degree of crystallinity the alternating material has the higher E, whereas the random copolymer would have a higher E value on the basis of degree of crosslinking.

(b) Yes, it is possible. The linear and isotactic polypropylene will have a greater tensile modulus. Linear polymers are more likely to crystallize that branched ones. The likelihood of crystallization for both syndiotactic and isotactic polypropylene is about the same, and, therefore, degree is crystallization is not a factor. Furthermore, tensile modulus is relatively insensitive to degree of polymerization (i.e., molecular weight)—the fact that branched PP has the higher molecular weight is not important.

(c) No, it is not possible. Linear polymers have higher degrees of crystallization (and higher tensile moduli) than branched polymers—on this basis, the PVC material should have the higher value of E. On the other hand, PVC has a more complex repeat unit structure than does polyethylene, which means that, on this basis, the PE would have a higher degree of crystallinity and also a greater tensile modulus. Also, tensile modulus is relatively independent of number-average molecular weight. Therefore, this determination is not possible since it is not possible to determine which of the two materials has the greater degree of crystallinity.

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15.20 *For each of the following pairs of polymers, do the following: (1) state whether or not it is possible to decide whether one polymer has a higher tensile strength than the other; (2) if this is possible, note which has the higher tensile strength and then cite the reason(s) for your choice; and (3) if it is not possible to decide, then state why.*

(a) Syndiotactic polystyrene having a number-average molecular weight of 600,000 g/mol; atactic polystyrene having a number-average molecular weight of 500,000 g/mol

(b) Random acrylonitrile-butadiene copolymer with 10% of possible sites crosslinked; block acrylonitrile-butadiene copolymer with 5% of possible sites crosslinked

(c) Network polyester; lightly branched polypropylene

Solution

For each of three pairs of polymers, we are to do the following: (1) determine whether or not it is possible to decide which has the higher tensile strength; (2) if it is possible, then note which has the higher tensile strength and then state the reasons for this choice; and (3) if it is not possible to decide, to state why.

(a) Yes it is possible. The syndiotactic polystyrene has the higher tensile strength. Syndiotactic polymers are more likely to crystallize than atactic ones; the greater the crystallinity, the higher the tensile strength. Furthermore, the syndiotactic also has a higher molecular weight; increasing molecular weight also enhances the strength.

(b) No it is not possible. The random acrylonitrile-butadiene copolymer has more crosslinking; increased crosslinking leads to an increase in strength. However, the block copolymeric material will most likely have a higher degree of crystallinity; and increasing crystallinity improves the strength.

(c) Yes it is possible. The network polyester will display a greater tensile strength. Relative chain motion is much more restricted than for the lightly branched polypropylene since there are many more of the strong covalent bonds for the network structure.

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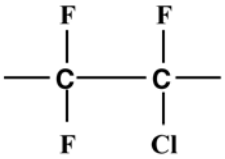
15.21 *Would you expect the tensile strength of polychlorotrifluoroethylene to be greater than, the same as, or less than that of a polytetrafluoroethylene specimen having the same molecular weight and degree of crystallinity? Why?*

Solution

The strength of a polychlorotrifluoroethylene having the repeat unit structure



will be greater than for a polytetrafluoroethylene having the same molecular weight and degree of crystallinity. The replacement of one fluorine atom within the PTFE repeat unit with a chlorine atom leads to a higher interchain attraction, and, thus, a stronger polymer. Furthermore, poly(vinyl chloride) is stronger than polyethylene (Table 15.1) for the same reason.

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15.22 *For each of the following pairs of polymers, plot and label schematic stress–strain curves on the same graph [i.e., make separate plots for parts (a), (b), and (c)].*

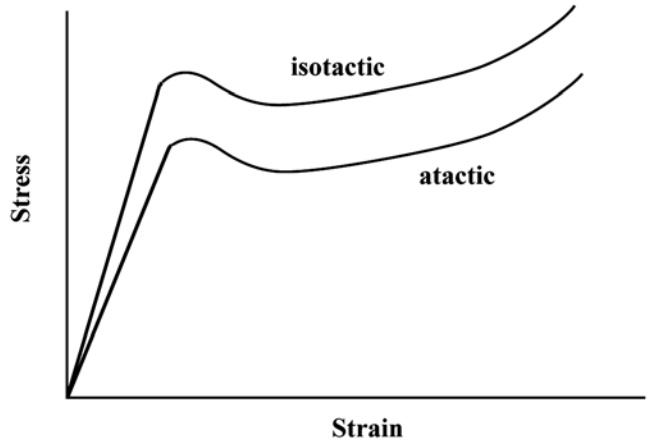
(a) Isotactic and linear polypropylene having a weight-average molecular weight of 120,000 g/mol; atactic and linear polypropylene having a weight-average molecular weight of 100,000 g/mol

(b) Branched poly(vinyl chloride) having a degree of polymerization of 2000; heavily crosslinked poly(vinyl chloride) having a degree of polymerization of 2000

(c) Poly(styrene-butadiene) random copolymer having a number-average molecular weight of 100,000 g/mol and 10% of the available sites crosslinked and tested at 20°C; poly(styrene-butadiene) random copolymer having a number-average molecular weight of 120,000 g/mol and 15% of the available sites crosslinked and tested at -85°C. Hint: poly(styrene-butadiene) copolymers may exhibit elastomeric behavior.

Solution

(a) Shown below are the stress-strain curves for the two polypropylene materials. These materials will display the stress-strain behavior of a normal plastic, curve *B* in Figure 15.1. However, the isotactic/linear will have a higher degree of crystallinity (since isotactic are more likely to crystallize than atactic/linear), and therefore, will have a higher tensile modulus and strength. Furthermore, the isotactic/linear also has a higher molecular weight which also leads to an increase in strength.



(b) Shown below are the stress-strain curves for the two polyvinyl chloride materials. The branched PVC will probably display the stress-strain behavior of a plastic, curve *B* in Figure 15.1. However, the heavily crosslinked PVC will undoubtedly have a higher tensile modulus, and, also a higher strength, and will most likely fail in a brittle manner--as curve *A*, Figure 15.1; these are the typical characteristics of a heavily crosslinked polymer.

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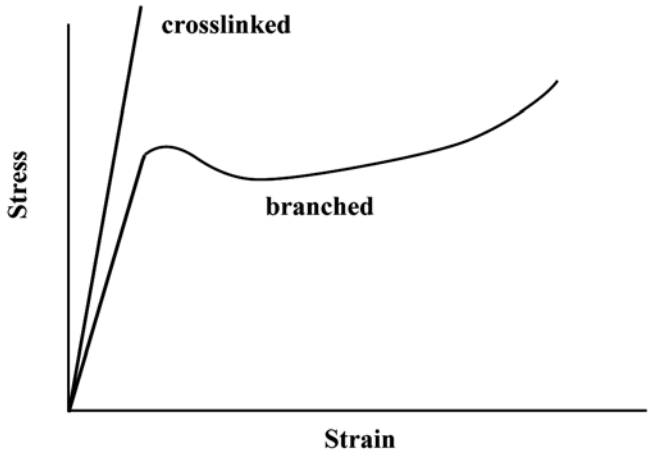
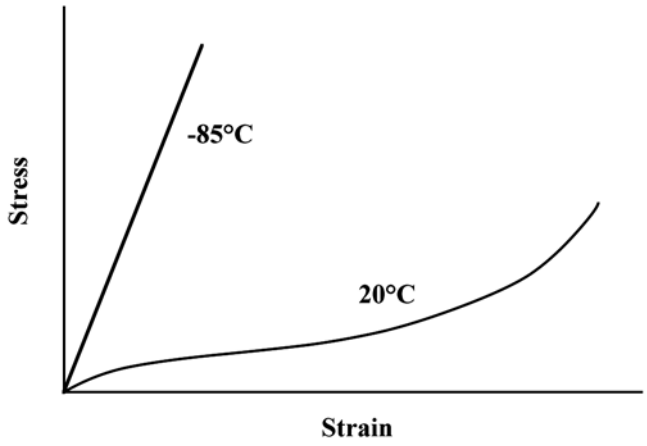


(c) Shown below are the stress-strain curves for the two poly(styrene-butadiene) random copolymers. The copolymer tested at 20°C will display elastomeric behavior (curve *C* of Figure 15.1) inasmuch as it is a random copolymer that is lightly crosslinked; furthermore, the temperature of testing is above its glass transition temperature. On the other hand, since -85°C is below the glass transition temperature of the poly(styrene-butadiene) copolymer, the stress-strain behavior under these conditions is as curve *A* of Figure 15.1.



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15.23 *List the two molecular characteristics that are essential for elastomers.*

Solution

Two molecular characteristics essential for elastomers are: (1) they must be amorphous, having chains that are extensively coiled and kinked in the unstressed state; and (2) there must be some crosslinking.

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15.24 *Which of the following would you expect to be elastomers and which thermosetting polymers at room temperature? Justify each choice.*

(a) Epoxy having a network structure

(b) Lightly crosslinked poly(styrene-butadiene) random copolymer that has a glass-transition temperature of -50°C

(c) Lightly branched and semicrystalline polytetrafluoroethylene that has a glass-transition temperature of -100°C

(d) Heavily crosslinked poly(ethylene-propylene) random copolymer that has a glass-transition temperature of 0°C

(e) Thermoplastic elastomer that has a glass-transition temperature of 75°C

Solution

This question asks us to choose from a list of materials those that would be expected to be elastomers and those that would be thermosetting polymers.

(a) Epoxy having a network structure will be a thermoset polymer since it has a network structure. It would not be an elastomer since it does not have a crosslinked chain structure.

(b) A lightly crosslinked poly(styrene-butadiene) random copolymer that has a glass-transition temperature of -50°C will be an elastomer since it 1) is a random copolymer, 2) is lightly crosslinked, and 3) is being used at a temperature above its glass transition. All three of these criteria are requisites for an elastomer.

(c) Lightly branched and semicrystalline PTFE would be neither an elastomer nor a thermoset. It is not crosslinked nor does it have a network structure.

(d) A heavily crosslinked poly(ethylene-propylene) random copolymer would be a thermoset inasmuch as it is heavily crosslinked.

(e) A thermoplastic elastomer that has a glass-transition temperature of 75°C is neither an elastomer nor a thermoset. Since it is a thermoplastic it is not a thermoset. Furthermore, room temperature is below its glass-transition temperature, and, therefore, it will not display elastomeric behavior.

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15.25 *Ten kilogram of polybutadiene is vulcanized with 4.8 kg sulfur. What fraction of the possible crosslink sites is bonded to sulfur crosslinks, assuming that, on the average, 4.5 sulfur atoms participate in each crosslink?*

Solution

This problem asks that we compute the fraction of possible crosslink sites in 10 kg of polybutadiene when 4.8 kg of S is added, assuming that, on the average, 4.5 sulfur atoms participate in each crosslink bond. Given the butadiene repeat unit in Table 14.5, we may calculate its molecular weight as follows:

$$A(\text{butadiene}) = 4(A_C) + 6(A_H)$$

$$= (4)(12.01\ \text{g/mol}) + 6(1.008\ \text{g/mol}) = 54.09\ \text{g/mol}$$

Which means that in 10 kg of butadiene there are $\dfrac{10{,}000\ \text{g}}{54.09\ \text{g/mol}} = 184.9\ \text{mol} = n_{\text{buta}}$.

For the vulcanization polybutadiene, there are two possible crosslink sites per repeat unit--one for each of the two carbon atoms that are doubly bonded. Furthermore, each of these crosslinks forms a bridge between two repeat units. Therefore, we can say that there is the equivalent of one crosslink per repeat unit. Let us now calculate the number of moles of sulfur (n_{sulfur}) that react with the butadiene, by taking the mole ratio of sulfur to butadiene, and then dividing this ratio by 4.5 atoms per crosslink; this yields the fraction of possible sites that are crosslinked. Thus

$$n_{\text{sulfur}} = \frac{4800\ \text{g}}{32.06\ \text{g/mol}} = 149.7\ \text{mol}$$

And

$$\text{fraction sites crosslinked} = \frac{\dfrac{n_{\text{sulfur}}}{n_{\text{buta}}}}{4.5} = \frac{\dfrac{149.7\ \text{mol}}{184.9\ \text{mol}}}{4.5} = 0.180$$

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15.26 *Compute the weight percent sulfur that must be added to completely crosslink an alternating chloroprene-acrylonitrile copolymer, assuming that five sulfur atoms participate in each crosslink.*

Solution

For an alternating chloroprene-acrylonitrile copolymer, we are asked to compute the weight percent sulfur necessary for complete crosslinking, assuming that, on the average, five sulfur atoms participate in each crosslink. The chloroprene and acrylonitrile repeat units are shown in Table 14.5, from which it may be noted that there are two possible crosslink sites on each chloroprene repeat unit (one site at each of the two carbon atoms that are doubly bonded), and no possible sites for acrylonitrile; also, since it is an alternating copolymer, the ratio of chloroprene to acrylonitrile repeat units is 1:1. Thus, for each pair of combined chloroprene-acrylonitrile repeat units that crosslink, ten sulfur atoms are required, or, for complete crosslinking, the sulfur-to-(chloroprene-acrylonitrile) ratio is 5:1.

Now, let us consider as our basis, one mole of the combined chloroprene-acrylonitrile repeat unit. In order for complete crosslinking, five moles of sulfur are required. Thus, for us to convert this composition to weight percent, it is necessary to convert moles to mass. The acrylonitrile repeat unit consists of three carbon atoms, three hydrogen atoms, and one nitrogen atom; the chloroprene repeat unit is composed of four carbons, five hydrogens, and one chlorine. This gives a molecular weight for the combined repeat unit of

$$m(\text{chloroprene-acrylonitrile}) = 3(A_C) + 3(A_H) + A_N + 4(A_C) + 5(A_H) + A_{Cl}$$

$$= 7(12.01\ \text{g/mol}) + 8(1.008\ \text{g/mol}) + 14.007\ \text{g/mol} + 35.45\ \text{g/mol} = 141.59\ \text{g/mol}$$

Or, in one mole of this combined repeat unit, there are 141.59 g. Furthermore, for complete crosslinking 5.0 mol of sulfur is required, which amounts to (5.0 mol)(32.06 g/mol) = 160.3 g. Thus, the concentration of S in weight percent C_S is just

$$C_S = \frac{160.3\ \text{g}}{160.3\ \text{g} + 141.59\ \text{g}} \times 100 = 53.1\ \text{wt\%}$$

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15.27 *The vulcanization of polyisoprene is accomplished with sulfur atoms according to Equation 15.4. If 57 wt% sulfur is combined with polyisoprene, how many crosslinks will be associated with each isoprene repeat unit if it is assumed that, on the average, six sulfur atoms participate in each crosslink?*

Solution

This problem asks for us to determine how many crosslinks form per isoprene repeat unit when 57 wt% sulfur is added. If we arbitrarily consider 100 g of the vulcanized material, 57 g will be sulfur and 43 g will be polyisoprene. Next, let us find how many moles of sulfur and isoprene correspond to these masses. The atomic weight of sulfur is 32.06 g/mol, and thus,

$$\#\ \text{moles S} = \frac{57\ \text{g}}{32.06\ \text{g/mol}} = 1.78\ \text{mol}$$

Now, in each isoprene repeat unit there are five carbon atoms and eight hydrogen atoms. Thus, the molecular weight of a mole of isoprene units is

$$(5)(12.01\ \text{g/mol}) + (8)(1.008\ \text{g/mol}) = 68.11\ \text{g/mol}$$

Or, in 43 g of polyisoprene, the number of moles is equal to

$$\#\ \text{moles isoprene} = \frac{43\ \text{g}}{68.11\ \text{g/mol}} = 0.631\ \text{mol}$$

Therefore, the ratio of moles of S to the number of moles of polyisoprene is

$$\frac{1.78\ \text{mol}}{0.631\ \text{mol}} : 1 = 2.82 : 1$$

When all possible sites are crosslinked, the ratio of the number of moles of sulfur to the number of moles of isoprene is 6:1; this is because there are two crosslink sites per repeat unit and each crosslink is shared between repeat units on adjacent chains, and there are 6 sulfur atoms per crosslink. Finally, to determine the fraction of sites that are crosslinked, we just divide the actual crosslinked sulfur/isoprene ratio by the completely crosslinked ratio. Or,

$$\text{fraction of repeat unit sites crosslinked} = \frac{2.82/1}{6/1} = 0.470$$

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15.28 *For the vulcanization of polyisoprene, compute the weight percent of sulfur that must be added to ensure that 8% of possible sites will be crosslinked; assume that, on the average, three sulfur atoms are associated with each crosslink.*

Solution

We are asked what weight percent of sulfur must be added to polyisoprene in order to ensure that 8% of possible sites are crosslinked, assuming that, on the average, three sulfur atoms are associated with each crosslink. Table 14.5 shows the repeat unit for cis-isoprene. For each of these units there are two possible crosslink sites; one site is associated with each of the two carbon atoms that are involved in the chain double bond. Since 8% of the possible sites are crosslinked, for each 100 isoprene repeat units 8 of them are crosslinked; actually there are two crosslink sites per repeat unit, but each crosslink is shared by two chains. Furthermore, on the average we assume that each crosslink is composed of 3 sulfur atoms; thus, there must be 3 × 8 or 24 sulfur atoms added for every 100 isoprene repeat units. In terms of moles, it is necessary to add 24 moles of sulfur to 100 moles of isoprene. The atomic weight of sulfur is 32.06 g/mol, while the molecular weight of isoprene is

$$A(\text{isoprene}) = 5(A_C) + 8(A_H)$$

$$= (5)(12.01\ \text{g/mol}) + (8)(1.008\ \text{g/mol}) = 68.11\ \text{g/mol}$$

The mass of sulfur added (m_S) is

$$m_S = (24\ \text{mol})(32.06\ \text{g/mol}) = 769.4\ \text{g}$$

While for isoprene

$$m_{ip} = (100\ \text{mol})(68.11\ \text{g/mol}) = 6811\ \text{g}$$

Or, the concentration of sulfur in weight percent (Equation 4.3) is just

$$C_S = \frac{m_S}{m_S + m_{ip}} \times 100 = \frac{769.4\ \text{g}}{769.4\ \text{g} + 6811\ \text{g}} \times 100 = 10.1\ \text{wt\%}$$

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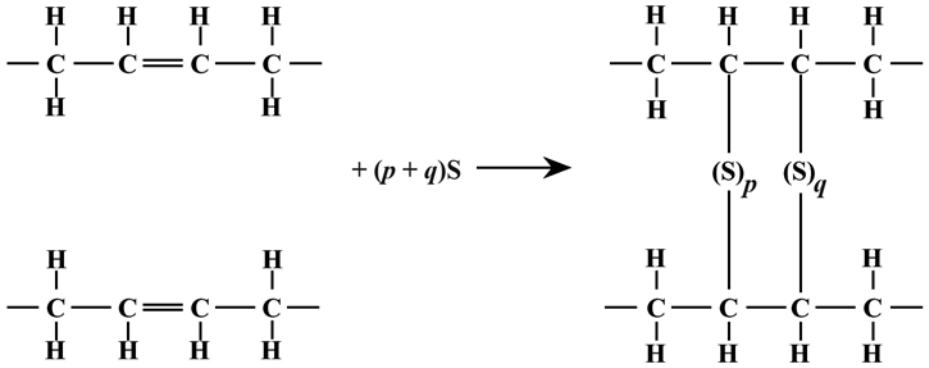
15.29 *Demonstrate, in a manner similar to Equation 15.4, how vulcanization may occur in a butadiene rubber.*

Solution

The reaction by which a butadiene rubber may become vulcanized is as follows:



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Crystallization

15.30 *Determine values for the constants n and k (Equation 10.17) for the crystallization of polypropylene (Figure 15.17) at 160°C.*

Solution

In this problem we are asked to determine the values of the constants n and k (Equation 10.17) for the crystallization of polypropylene at 160°C (Figure 15.17). One way to solve this problem is to take two values of percent recrystallization (which is just 100y, Equation 10.17) and their corresponding time values, then set up two simultaneous equations, from which n and k may be determined. In order to expedite this process, we will rearrange and do some algebraic manipulation of Equation 10.17. First of all, we rearrange as follows:

$$1 - y = \exp\left(-kt^n\right)$$

Now taking natural logarithms

$$\ln (1 - y) = -kt^n$$

Or

$$-\ln (1 - y) = kt^n$$

which may also be expressed as

$$\ln\left(\frac{1}{1 - y}\right) = kt^n$$

Now taking natural logarithms again, leads to

$$\ln\left[\ln\left(\frac{1}{1 - y}\right)\right] = \ln k + n \ln t$$

which is the form of the equation that we will now use. From the 160°C curve of Figure 15.17, let us arbitrarily choose two percent crystallized values of 20% and 80% (i.e., $y_1 = 0.20$ and $y_2 = 0.80$). The corresponding time

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values are t_1 = 3400 min and t_2 = 6700 min (realizing that the time axis is scaled logarithmically). Thus, our two simultaneous equations become

$$\ln\left[\ln\left(\frac{1}{1-0.20}\right)\right] = \ln k + n \ln(3400)$$

$$\ln\left[\ln\left(\frac{1}{1-0.80}\right)\right] = \ln k + n \ln(6700)$$

from which we obtain the values $n = 2.91$ and $k = 1.182 \times 10^{-11}$.

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Melting and Glass Transition Temperatures

15.31 *Name the following polymer(s) that would be suitable for the fabrication of cups to contain hot coffee: polyethylene, polypropylene, poly(vinyl chloride), PET polyester, and polycarbonate. Why?*

Solution

This question asks us to name which, of several polymers, would be suitable for the fabrication of cups to contain hot coffee. At its glass transition temperature, an amorphous polymer begins to soften. The maximum temperature of hot coffee is probably slightly below 100°C (212°F). Of the polymers listed, only polystyrene and polycarbonate have glass transition temperatures of 100°C or above (Table 15.2), and would be suitable for this application.

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15.32 *Of those polymers listed in Table 15.2, which polymer(s) would be best suited for use as ice cube trays? Why?*

Solution

In order for a polymer to be suited for use as an ice cube tray it must have a glass-transition temperature below 0°C. Of those polymers listed in Table 15.2 only low-density and high-density polyethylene, PTFE, and polypropylene satisfy this criterion.

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Factors That Influence Melting and Glass Transition Temperatures

15.33 *For each of the following pairs of polymers, plot and label schematic specific volume versus temperature curves on the same graph [i.e., make separate plots for parts (a), (b), and (c)].*

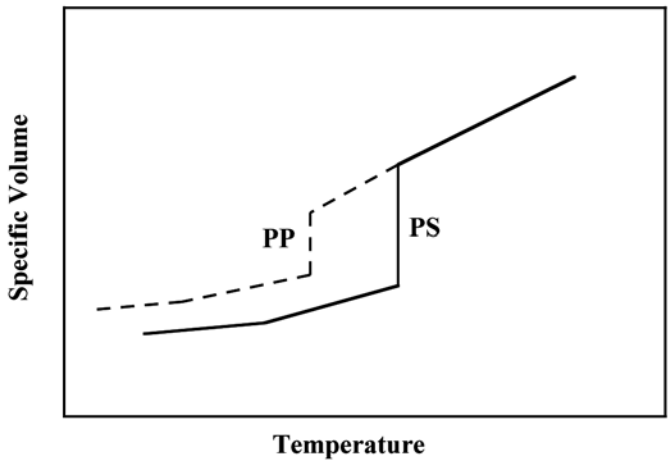
(a) Spherulitic polypropylene, of 25% crystallinity, and having a weight-average molecular weight of 75,000 g/mol; spherulitic polystyrene, of 25% crystallinity, and having a weight-average molecular weight of 100,000 g/mol

(b) Graft poly(styrene-butadiene) copolymer with 10% of available sites crosslinked; random poly(styrene-butadiene) copolymer with 15% of available sites crosslinked

(c) Polyethylene having a density of 0.985 g/cm^3 and a degree of polymerization of 2500; polyethylene having a density of 0.915 g/cm^3 and a degree of polymerization of 2000

Solution

(a) Shown below are the specific volume-versus-temperature curves for the polypropylene and polystyrene materials. Since both polymers are 25% crystalline, they will exhibit behavior similar to curve *B* in Figure 15.18. However, polystyrene will have higher melting and glass transition temperatures due to the bulkier side group in its repeat unit structure, and since it has a higher weight-average molecular weight.



(b) Shown below are the specific volume-versus-temperature curves for the graft and random poly(styrene-butadiene) copolymers. Since these materials are graft and random copolymers, both will be highly noncrystalline, and, thus, will display the behavior similar to curve *A* in Figure 15.18. However, since the random has the greater degree of crosslinking, it will also have the higher glass transition temperature.

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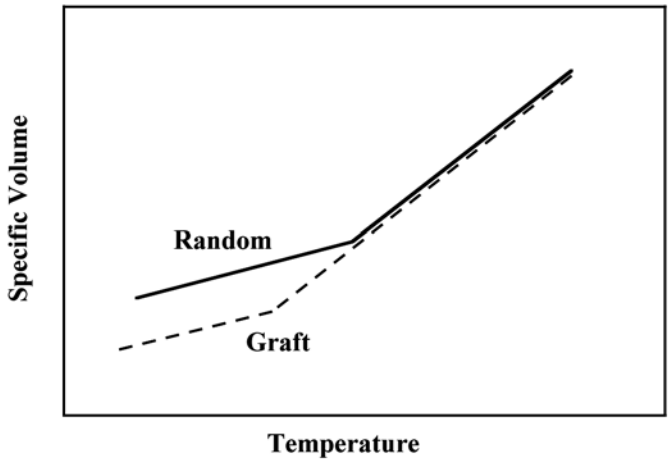
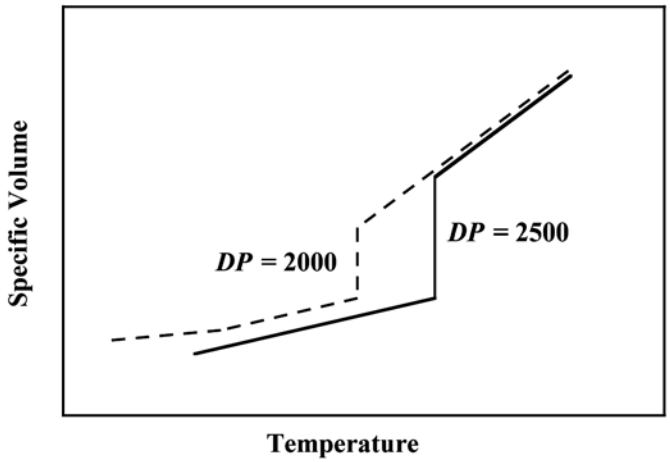


(c) Shown below are the specific volume-versus-temperature curves for the two polyethylene materials. The polyethylene having a density of 0.985 g/cm^3 will be highly crystalline, and, thus, will exhibit a behavior similar to curve *C* in Figure 15.18. On the other hand, the other material, of lower density will have some branching and also be semicrystalline; thus, its behavior will be similar to curve *B* of Figure 15.18. In addition, the melting temperature of the higher density material will be greater since it has less branching and a higher degree of polymerization.



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15.34 *For each of the following pairs of polymers, do the following: (1) state whether or not it is possible to determine whether one polymer has a higher melting temperature than the other; (2) if it is possible, note which has the higher melting temperature and then cite reason(s) for your choice; and (3) if it is not possible to decide, then state why.*

(a) Isotactic polystyrene that has a density of 1.12 g/cm^3 and a weight-average molecular weight of 150,000 g/mol; syndiotactic polystyrene that has a density of 1.10 g/cm^3 and a weight-average molecular weight of 125,000 g/mol

(b) Linear polyethylene that has a degree of polymerization of 5,000; linear and isotactic polypropylene that has a degree of polymerization of 6,500

(c) Branched and isotactic polystyrene that has a degree of polymerization of 4,000; linear and isotactic polypropylene that has a degree of polymerization of 7,500

Solution

(a) Yes, it is possible to determine which of the two polystyrenes has the higher T_m. The isotactic polystyrene will have the higher melting temperature because it has a higher density (i.e., less branching) and also the greater weight-average molecular weight.

(b) Yes, it is possible to determine which polymer has the higher melting temperature. The polypropylene will have the higher T_m because it has a bulky phenyl side group in its repeat unit structure, which is absent in the polyethylene. Furthermore, the polypropylene has a higher degree of polymerization.

(c) No, it is not possible to determine which of the two polymers has the higher melting temperature. The polystyrene has a bulkier side group than the polypropylene; on the basis of this effect alone, the polystyrene should have the greater T_m. However, the polystyrene has more branching and a lower degree of polymerization; both of these factors lead to a lowering of the melting temperature.

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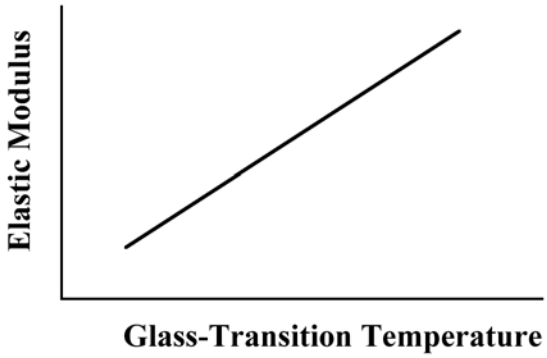
15.35 *Make a schematic plot showing how the modulus of elasticity of an amorphous polymer depends on the glass transition temperature. Assume that molecular weight is held constant.*

Solution

For an amorphous polymer, the elastic modulus may be enhanced by increasing the number of crosslinks (while maintaining the molecular weight constant); this will also enhance the glass transition temperature. Thus, the modulus-glass transition temperature behavior would appear as



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Elastomers

Fibers

Miscellaneous Applications

15.36 *Briefly explain the difference in molecular chemistry between silicone polymers and other polymeric materials.*

Solution

The backbone chain of most polymers consists of carbon atoms that are linked together. For the silicone polymers, this backbone chain is composed of silicon and oxygen atoms that alternate positions.

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15.37 *List two important characteristics for polymers that are to be used in fiber applications.*

Solution

Two important characteristics for polymers that are to be used in fiber applications are: (1) they must have high molecular weights, and (2) they must have chain configurations/structures that will allow for high degrees of crystallinity.

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15.38 *Cite five important characteristics for polymers that are to be used in thin-film applications.*

Solution

Five important characteristics for polymers that are to be used in thin-film applications are: (1) low density; (2) high flexibility; (3) high tensile and tear strengths; (4) resistance to moisture/chemical attack; and (5) low gas permeability.

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Polymerization

15.39 *Cite the primary differences between addition and condensation polymerization techniques.*

Solution

For addition polymerization, the reactant species have the same chemical composition as the monomer species in the molecular chain. This is not the case for condensation polymerization, wherein there is a chemical reaction between two or more monomer species, producing the repeating unit. There is often a low molecular weight by-product for condensation polymerization; such is not found for addition polymerization.

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15.40 (*a) How much ethylene glycol must be added to 47.3 kg of terephthalic acid to produce a linear chain structure of poly(ethylene terephthalate) according to Equation 15.9?*

(b) What is the mass of the resulting polymer?

Solution

(a) This problem asks that we determine how much ethylene glycol must be added to 47.3 kg of terephthalic acid to produce a linear chain structure of poly(ethylene terephthalate) according to Equation 15.9. Since the chemical formulas are provided in this equation we may calculate the molecular weights of each of these materials as follows:

$$MW(\text{ethylene glycol}) = 2(A_C) + 6(A_H) + 2(A_O)$$

$$= 2(12.01\ \text{g/mol}) + 6(1.008\ \text{g/mol}) + 2(16.00\ \text{g/mol}) = 62.07\ \text{g/mol}$$

$$MW(\text{terephthalic acid}) = 8(A_C) + 6(A_H) + 4(A_O)$$

$$= 8\ (12.01\ \text{g/mol}) + 6(1.008\ \text{g/mol}) + 4(16.00\ \text{g/mol}) = 166.13\ \text{g/mol}$$

The 47.3 kg mass of terephthalic acid equals 47,300 g or $\frac{47{,}300\ \text{g}}{166.13\ \text{g/mol}} = 284.72$ mol. Since, according to Equation 15.9, each mole of terephthalic acid used requires one mole of ethylene glycol, which is equivalent to (284.72 mol)(62.07 g/mol) = 17,673 g = 17.673 kg.

(b) Now we are asked for the mass of the resulting polymer. Inasmuch as one mole of water is given off for every repeat unit produced, this corresponds to 284.72 moles or (284.72 mol)(18.02 g/mol) = 5130 g or 5.130 kg since the molecular weight of water is 18.02 g/mol. The mass of poly(ethylene terephthalate) is just the sum of the masses of the two reactant materials [as computed in part (a)] minus the mass of water released, or

$$\text{mass [poly(ethylene terephthalate)]} = 47.300\ \text{kg} + 17.673\ \text{kg} - 5.130\ \text{kg} = 59.843\ \text{kg}$$

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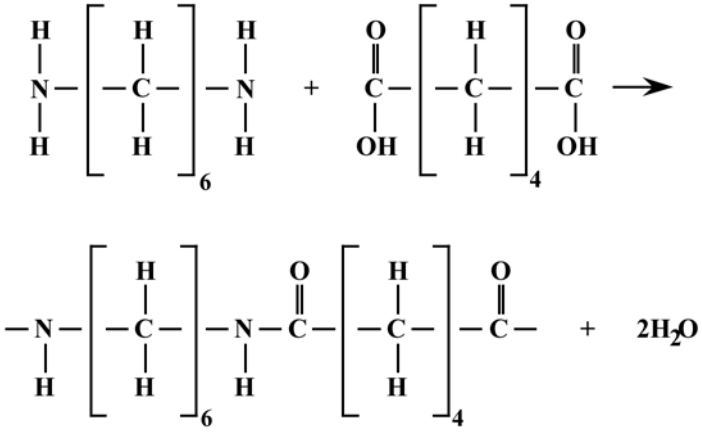
15.41 *Nylon 6,6 may be formed by means of a condensation polymerization reaction in which hexamethylene diamine [$NH_2—(CH_2)_6—NH_2$] and adipic acid react with one another with the formation of water as a byproduct. What masses of hexamethylene diamine and adipic acid are necessary to yield 37.5 kg of completely linear nylon 6,6? (Note: the chemical equation for this reaction is the answer to Concept Check 15.12.)*

Solution

This problem asks for us to calculate the masses of hexamethylene diamine and adipic acid necessary to yield 37.5 kg of completely linear nylon 6,6. The chemical equation for this reaction is the answer to Concept Check 15.12, which is as follows:



From this equation we may calculate the molecular weights of these molecules.

$$MW(\text{adipic}) = 6(A_C) + 10(A_H) + 4(A_O)$$

$$= 6(12.01\ \text{g/mol}) + 10(1.008\ \text{g/mol}) + 4(16.00\ \text{g/mol}) = 146.14\ \text{g/mol}$$

$$MW(\text{hexamethylene}) = 6(A_C) + 16(A_H) + 2(A_N)$$

$$= 6(12.01\ \text{g/mol}) + 16(1.008\ \text{g/mol}) + 2(14.01\ \text{g/mol}) = 116.21\ \text{g/mol}$$

$$MW(\text{nylon}) = 12(A_C) + 22(A_H) + 2(A_N) + 2(A_O)$$

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$$= 12(12.01\ \text{g/mol}) + 22(1.008\ \text{g/mol}) + 2(14.01\ \text{g/mol}) + 2(16.00\ \text{g/mol})$$

$$= 226.32\ \text{g/mol}$$

The mass of 37.5 kg of nylon 6,6 equals 37,500 g or

$$m(\text{nylon}) = \frac{37{,}500\ \text{g}}{226.32\ \text{g/mol}} = 165.7\ \text{mol}$$

Since, according to the chemical equation given above, each mole of nylon 6,6 that is produced requires one mole each of adipic acid and hexamethylene diamine, with two moles of water as the by-product. The masses corresponding to 165.7 moles of adipic acid and hexamethylene diamine are as follows:

$$m(\text{adipic}) = (165.7\ \text{mol})(146.14\ \text{g/mol}) = 24{,}215\ \text{g} = 24.215\ \text{kg}$$

$$m(\text{hexamethylene}) = (165.7\ \text{mol})(116.21\ \text{g/mol}) = 19{,}256\ \text{g} = 19.256\ \text{kg}$$

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Polymer Additives

15.42 *What is the distinction between dye and pigment colorants?*

Solution

The distinction between dye and pigment colorants is that a dye dissolves within and becomes a part of the polymer structure, whereas a pigment does not dissolve, but remains as a separate phase.

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Forming Techniques for Plastics

15.43 *Cite four factors that determine what fabrication technique is used to form polymeric materials.*

Solution

Four factors that determine what fabrication technique is used to form polymeric materials are: (1) whether the polymer is thermoplastic or thermosetting; (2) if thermoplastic, the softening temperature; (3) atmospheric stability; and (4) the geometry and size of the finished product.

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15.44 *Contrast compression, injection, and transfer molding techniques that are used to form plastic materials.*

Solution

This question requests that we compare polymer molding techniques. For compression molding, both heat and pressure are applied after the polymer and necessary additives are situated between the mold members. For transfer molding, the solid materials (normally thermosetting in nature) are first melted in the transfer chamber prior to being forced into the die. And, for injection molding (normally used for thermoplastic materials), the raw materials are impelled by a ram through a heating chamber, and finally into the die cavity.

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Fabrication of Fibers and Films

15.45 *Why must fiber materials that are melt spun and then drawn be thermoplastic? Cite two reasons.*

Solution

Fiber materials that are melt spun must be thermoplastic because: (1) In order to be melt spun, they must be capable of forming a viscous liquid when heated, which is not possible for thermosets. (2) During drawing, mechanical elongation must be possible; inasmuch as thermosetting materials are, in general, hard and relatively brittle, they are not easily elongated.

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15.46 *Which of the following polyethylene thin films would have the better mechanical characteristics: (1) formed by blowing, or (2) formed by extrusion and then rolled? Why?*

Solution

Of the two polymers cited, the one that was formed by extrusion and then rolled would have the higher strength. Both blown and extruded materials would have roughly comparable strengths; however the rolling operation would further serve to enhance the strength of the extruded material.

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DESIGN QUESTIONS

15.D1 *(a) List several advantages and disadvantages of using transparent polymeric materials for eyeglass lenses.*

(b) Cite four properties (in addition to being transparent) that are important for this application.

(c) Note three polymers that may be candidates for eyeglass lenses, and then tabulate values of the properties noted in part (b) for these three materials.

Solution

(a) Several advantages of using transparent polymeric materials for eyeglass lenses are: they have relatively low densities, and, therefore, are light in weight; they are relatively easy to grind to have the desired contours; they are less likely to shatter than are glass lenses; wraparound lenses for protection during sports activities are possible; and they filter out more ultraviolet radiation than do glass lenses.

The principal disadvantage of these types of lenses is that some are relatively soft and are easily scratched (although antiscratch coatings may be applied). Plastic lenses are not as mechanically stable as glass, and, therefore, are not as precise optically.

(b) Some of the properties that are important for polymer lens materials are: they should be relatively hard in order to resist scratching; they must be impact resistant; they should be shatter resistant; they must have a relatively high index of refraction such that thin lenses may be ground for very nearsighted people; and they should absorb significant proportions of all types of ultraviolet radiation, which radiation can do damage to the eye tissues.

(c) Of those polymers discussed in this chapter and Chapter 14, likely lens candidates are polystyrene, poly(methyl methacrylate), and polycarbonate; these three materials are not easily crystallized, and, therefore, are normally transparent. Upon consultation of their fracture toughnesses (Table B.5 in Appendix B), polycarbonate is the most superior of the three.

Commercially, the two plastic lens materials of choice are polycarbonate and allyl diglycol carbonate (having the trade name CR-39). Polycarbonate is very impact resistant, but not as hard as CR-39. Furthermore, PC comes in both normal and high refractive-index grades.

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15.D2 *Write an essay on polymeric materials that are used in the packaging of food products and drinks. Include a list of the general requisite characteristics of materials that are used for these applications. Now cite a specific material that is utilized for each of three different container types and the rationale for each choice.*

Solution

There are three primary requirements for polymeric materials that are utilized in the packaging of food products and drinks; these are: (1) sufficient strength, to include tensile, tear, and impact strengths; (2) barrier protection--that is, being resistant to permeation by oxygen, water vapor, and carbon dioxide; and (3) being nonreactive with the food/drink contents--such reactions can compromise the integrity of the packaging material, or they can produce toxic by-products.

With regard to strength, poly(ethylene terephthalate) (PET or PETE) and oriented polypropylene (OPP) have high tensile strengths, linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) have high tear strengths, while those polymers having the best impact strengths are PET and poly(vinyl chloride) (PVC). Relative to barrier characteristics, ethylene vinyl alcohol (EVOH) and poly(vinylidene chloride) (PVDC) copolymers are relatively impermeable to oxygen and carbon dioxide, whereas high-density polyethylene (HDPE), PVDC, polypropylene, and LDPE are impervious to water vapor.

Most common polymers are relatively nonreactive with food products, and are considered safe; exceptions are acrylonitrile and plasticizers used in PVC materials.

The aesthetics of packaging polymers are also important in the marketing of food and drink products. Some will be colored, many are adorned with printing, others need to be transparent and clear, and many need to be resistant to scuffing.

On the basis of the preceding discussion, examples of polymers that are used for specific applications are as follows:

PET(E) for soda pop containers;

PVC for beer containers;

LDPE and HDPE films for packaging bread and bakery products.

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15.D3 *Write an essay on the replacement of metallic automobile components by polymers and composite materials. Address the following issues: (1) Which automotive components (e.g., crankshaft) now use polymers and/or composites? (2) Specifically what materials (e.g., high-density polyethylene) are now being used? (3) What are the reasons for these replacements?*

Solution

The primary reasons that the automotive industry has replaced metallic automobile components with polymer and composite materials are: polymers/composites (1) have lower densities, and afford higher fuel efficiencies; (2) may be produced at lower costs but with comparable mechanical characteristics; (3) are in many environments more corrosion resistant; (4) reduce noise, and (5) are thermally insulating and thus reduce the transference of heat.

These replacements are many and varied. Several are as follows:

Bumper fascia are molded from an elastomer-modified polypropylene.

Overhead consoles are made of poly(phenylene oxide) and recycled polycarbonate.

Rocker arm covers are injection molded of a glass- and mineral-reinforced nylon 6,6 composite.

Torque converter reactors, water outlets, pulleys, and brake pistons, are made from phenolic thermoset composites that are reinforced with glass fibers.

Air intake manifolds are made of a glass-reinforced nylon 6,6.

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CHAPTER 16

COMPOSITES

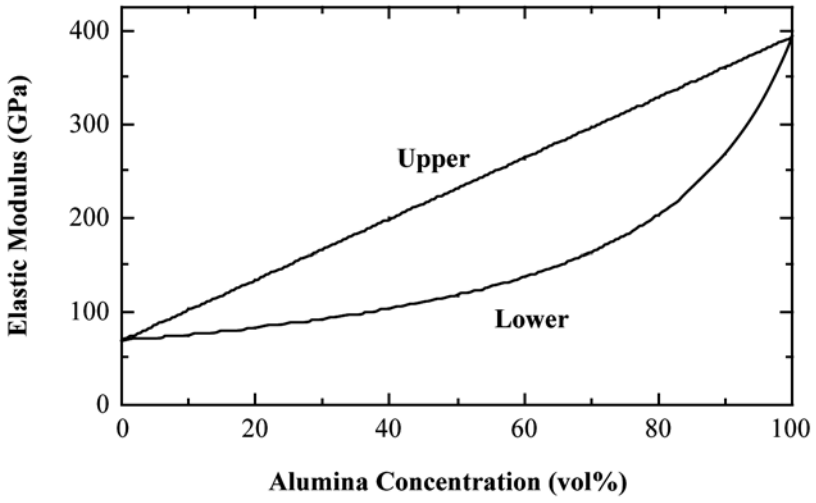
PROBLEM SOLUTIONS

Large-Particle Composites

16.1 *The mechanical properties of aluminum may be improved by incorporating fine particles of aluminum oxide (Al_2O_3). Given that the moduli of elasticity of these materials are, respectively, 69 GPa (10×10^6 psi) and 393 GPa (57×10^6 psi), plot modulus of elasticity versus the volume percent of Al_2O_3 in Al from 0 to 100 vol%, using both upper- and lower-bound expressions.*

Solution

The elastic modulus versus the volume percent of Al_2O_3 is shown below, on which is included both upper and lower bound curves; these curves were generated using Equations 16.1 and 16.2, respectively, and using the moduli of elasticity for aluminum and Al_2O_3 that were given in the problem statement.



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16.2 *Estimate the maximum and minimum thermal conductivity values for a cermet that contains 85 vol% titanium carbide (TiC) particles in a cobalt matrix. Assume thermal conductivities of 27 and 69 W/m-K for TiC and Co, respectively.*

Solution

This problem asks for the maximum and minimum thermal conductivity values for a TiC-Co cermet. Using a modified form of Equation 16.1 the maximum thermal conductivity k_{max} is calculated as

$$k_{max} = k_m V_m + k_p V_p = k_{Co} V_{Co} + k_{TiC} V_{TiC}$$

$$= (69 \text{ W/m - K})(0.15) + (27 \text{ W/m - K})(0.85) = 33.3 \text{ W/m - K}$$

Using a modified form of Equation 16.2, the minimum thermal conductivity k_{min} will be

$$k_{min} = \frac{k_{Co} k_{TiC}}{V_{Co} k_{TiC} + V_{TiC} k_{Co}}$$

$$= \frac{(69 \text{ W/m - K})(27 \text{ W/m - K})}{(0.15)(27 \text{ W/m - K}) + (0.85)(69 \text{ W/m - K})}$$

$$= 29.7 \text{ W/m-K}$$

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16.3 *A large-particle composite consisting of tungsten particles within a copper matrix is to be prepared. If the volume fractions of tungsten and copper are 0.60 and 0.40, respectively, estimate the upper limit for the specific stiffness of this composite given the data that follow.*

	Specific Gravity	***Modulus of Elasticity (GPa)***
Copper	*8.9*	*110*
Tungsten	*19.3*	*407*

Solution

Given the elastic moduli and specific gravities for copper and tungsten we are asked to estimate the upper limit for specific stiffness when the volume fractions of tungsten and copper are 0.60 and 0.40, respectively. There are two approaches that may be applied to solve this problem. The first is to estimate both the upper limits of elastic modulus [$E_c(u)$] and specific gravity (ρ_c) for the composite, using expressions of the form of Equation 16.1, and then take their ratio. Using this approach

$$E_c(u) = E_{Cu}V_{Cu} + E_WV_W$$

$$= (110\ \text{GPa})(0.40) + (407\ \text{GPa})(0.60)$$

$$= 288\ \text{GPa}$$

And

$$\rho_c = \rho_{Cu}V_{Cu} + \rho_WV_W$$

$$= (8.9)(0.40) + (19.3)(0.60) = 15.14$$

Therefore

$$\text{Specific Stiffness} = \frac{E_c(u)}{\rho_c} = \frac{288\ \text{GPa}}{15.14} = 19.0\ \text{GPa}$$

With the alternate approach, the specific stiffness is calculated, again employing a modification of Equation 16.1, but using the specific stiffness-volume fraction product for both metals, as follows:

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$$\text{Specific Stiffness} = \frac{E_{\text{Cu}}}{\rho_{\text{Cu}}} V_{\text{Cu}} + \frac{E_{\text{W}}}{\rho_{\text{W}}} V_{\text{W}}$$

$$= \frac{110 \text{ GPa}}{8.9}(0.40) + \frac{407 \text{ GPa}}{19.3}(0.60) = 17.6 \text{ GPa}$$

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16.4 *(a) What is the distinction between cement and concrete?*

(b) Cite three important limitations that restrict the use of concrete as a structural material.

(c) Briefly explain three techniques that are utilized to strengthen concrete by reinforcement.

Solution

(a) Concrete consists of an aggregate of particles that are bonded together by a cement.

(b) Three limitations of concrete are: (1) it is a relatively weak and brittle material; (2) it experiences relatively large thermal expansions (contractions) with changes in temperature; and (3) it may crack when exposed to freeze-thaw cycles.

(c) Three reinforcement strengthening techniques are: (1) reinforcement with steel wires, rods, etc.; (2) reinforcement with fine fibers of a high modulus material; and (3) introduction of residual compressive stresses by prestressing or posttensioning.

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Dispersion-Strengthened Composites

16.5 *Cite one similarity and two differences between precipitation hardening and dispersion strengthening.*

Solution

The similarity between precipitation hardening and dispersion strengthening is the strengthening mechanism--i.e., the precipitates/particles effectively hinder dislocation motion.

The two differences are: (1) the hardening/strengthening effect is not retained at elevated temperatures for precipitation hardening--however, it is retained for dispersion strengthening; and (2) the strength is developed by a heat treatment for precipitation hardening--such is not the case for dispersion strengthening.

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Influence of Fiber Length

16.6 *For some glass fiber-epoxy matrix combination, the critical fiber length-fiber diameter ratio is 50. Using the data in Table 16.4, determine the fiber-matrix bond strength.*

Solution

This problem asks that, for a glass fiber-epoxy matrix combination, to determine the fiber-matrix bond strength if the critical fiber length-fiber diameter ratio is 50. Thus, we are to solve for τ_c in Equation 16.3. Since we are given that $\sigma_f^* = 3.45$ GPa from Table 16.4, and that $\frac{l_c}{d} = 50$, then

$$\tau_c = \sigma_f^* \left(\frac{d}{2 l_c} \right) = (3.45 \times 10^3 \text{ MPa}) \left(\frac{1}{2} \right) \left(\frac{1}{50} \right) = 34.5 \text{ MPa}$$

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16.7 *(a) For a fiber-reinforced composite, the efficiency of reinforcement η is dependent on fiber length l according to*

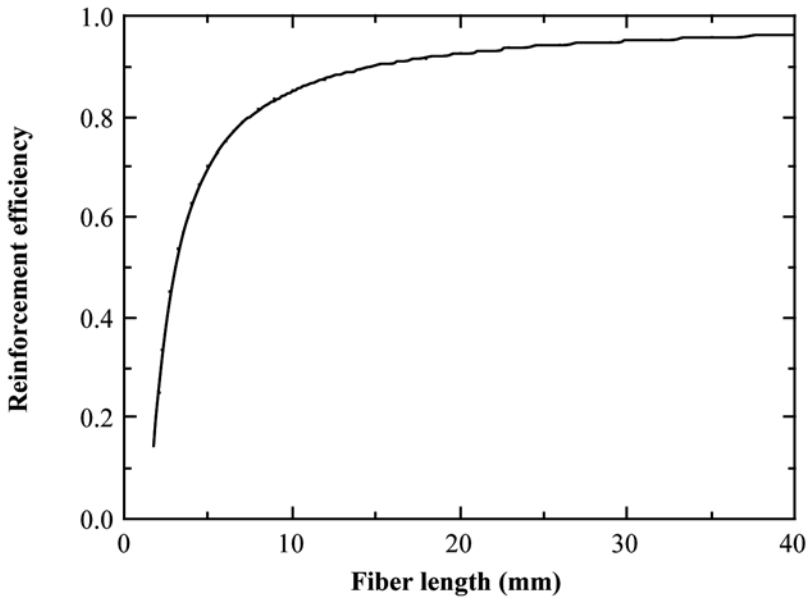
$$\eta = \frac{l - 2x}{l}$$

where x represents the length of the fiber at each end that does not contribute to the load transfer. Make a plot of η versus l to l = 40 mm (1.6 in.) assuming that x = 0.75 mm (0.03 in.).

(b) What length is required for a 0.80 efficiency of reinforcement?

Solution

(a) The plot of reinforcement efficiency versus fiber length is given below.



(b) This portion of the problem asks for the length required for a 0.80 efficiency of reinforcement. Solving for *l* from the given expression

$$l = \frac{2x}{1 - \eta}$$

Or, when $x = 0.75$ mm (0.03 in.) and $\eta = 0.80$, then

$$l = \frac{(2)(0.75 \text{ mm})}{1 - 0.80} = 7.5 \text{ mm} \quad (0.30 \text{ in.})$$

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Influence of Fiber Orientation and Concentration

16.8 *A continuous and aligned fiber-reinforced composite is to be produced consisting of 30 vol% aramid fibers and 70 vol% of a polycarbonate matrix; mechanical characteristics of these two materials are as follows:*

	***Modulus of Elasticity* [*GPa* (*psi*)]**	***Tensile Strength* [*MPa* (*psi*)]**
Aramid fiber	*131 (19×10^6)*	*3600 (520,000)*
Polycarbonate	*2.4 (3.5×10^5)*	*65 (9425)*

Also, the stress on the polycarbonate matrix when the aramid fibers fail is 45 MPa (6500 psi).

For this composite, compute

(a) the longitudinal tensile strength, and

(b) the longitudinal modulus of elasticity

Solution

This problem calls for us to compute the longitudinal tensile strength and elastic modulus of an aramid fiber-reinforced polycarbonate composite.

(a) The longitudinal tensile strength is determined using Equation 16.17 as

$$\sigma_{cl}^{*} = \sigma_{m}^{'}\left(1 - V_f\right) + \sigma_{f}^{*}V_f$$

$$= (45\ \text{MPa})(0.70) + (3600)(0.30)$$

$$= 1100\ \text{MPa}\ \ (160{,}000\ \text{psi})$$

(b) The longitudinal elastic modulus is computed using Equation 16.10a as

$$E_{cl} = E_m V_m + E_f V_f$$

$$= (2.4\ \text{GPa})(0.70) + (131\ \text{GPa})(0.30)$$

$$= 41\ \text{GPa}\ \ (5.95 \times 10^6\ \text{psi})$$

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16.9 *Is it possible to produce a continuous and oriented aramid fiber-epoxy matrix composite having longitudinal and transverse moduli of elasticity of 57.1 GPa (8.28×10^6 psi) and 4.12 GPa (6×10^5 psi), respectively? Why or why not? Assume that the modulus of elasticity of the epoxy is 2.4 GPa (3.50×10^5 psi).*

Solution

This problem asks for us to determine if it is possible to produce a continuous and oriented aramid fiber-epoxy matrix composite having longitudinal and transverse moduli of elasticity of 57.1 GPa and 4.12 GPa, respectively, given that the modulus of elasticity for the epoxy is 2.4 GPa. Also, from Table 16.4 the value of E for aramid fibers is 131 GPa. The approach to solving this problem is to calculate values of V_f for both longitudinal and transverse cases using the data and Equations 16.10b and 16.16; if the two V_f values are the same then this composite is possible.

For the longitudinal modulus E_{cl} (using Equation 16.10b),

$$E_{cl} = E_m(1 - V_{fl}) + E_f V_{fl}$$

$$57.1 \text{ GPa} = (2.4 \text{ GPa})(1 - V_{fl}) + (131 \text{ GPa})V_{fl}$$

Solving this expression for V_{fl} (i.e., the volume fraction of fibers for the longitudinal case) yields $V_{fl} = 0.425$.

Now, repeating this procedure for the transverse modulus E_{ct} (using Equation 16.16)

$$E_{ct} = \frac{E_m E_f}{(1 - V_{ft})E_f + V_{ft}E_m}$$

$$4.12 \text{ GPa} = \frac{(2.4 \text{ GPa})(131 \text{ GPa})}{(1 - V_{ft})(131 \text{ GPa}) + V_{ft}(2.4 \text{ GPa})}$$

Solving this expression for V_{ft} (i.e., the volume fraction of fibers for the transverse case), leads to $V_{ft} = 0.425$. Thus, since V_{fl} and V_{ft} are equal, the proposed composite *is possible*.

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16.10 *For a continuous and oriented fiber-reinforced composite, the moduli of elasticity in the longitudinal and transverse directions are 19.7 and 3.66 GPa (2.8×10^6 and 5.3×10^5 psi), respectively. If the volume fraction of fibers is 0.25, determine the moduli of elasticity of fiber and matrix phases.*

Solution

This problem asks for us to compute the elastic moduli of fiber and matrix phases for a continuous and oriented fiber-reinforced composite. We can write expressions for the longitudinal and transverse elastic moduli using Equations 16.10b and 16.16, as

$$E_{cl} = E_m(1 - V_f) + E_f V_f$$

$$19.7 \text{ GPa} = E_m(1 - 0.25) + E_f(0.25)$$

And

$$E_{ct} = \frac{E_m E_f}{(1 - V_f)E_f + V_f E_m}$$

$$3.66 \text{ GPa} = \frac{E_m E_f}{(1 - 0.25)E_f + 0.25E_m}$$

Solving these two expressions simultaneously for E_m and E_f leads to

$$E_m = 2.79 \text{ GPa} \quad (4.04 \times 10^5 \text{ psi})$$

$$E_f = 70.4 \text{ GPa} \quad (10.2 \times 10^6 \text{ psi})$$

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16.11 *(a) Verify that Equation 16.11, the expression for the fiber load–matrix load ratio (F_f/F_m), is valid. (b) What is the F_f/F_c ratio in terms of E_f, E_m, and V_f?*

Solution

(a) In order to show that the relationship in Equation 16.11 is valid, we begin with Equation 16.4—i.e.,

$$F_c = F_m + F_f$$

which may be manipulated to the form

$$\frac{F_c}{F_m} = 1 + \frac{F_f}{F_m}$$

or

$$\frac{F_f}{F_m} = \frac{F_c}{F_m} - 1$$

For elastic deformation, combining Equations 6.1 and 6.5

$$\sigma = \frac{F}{A} = \varepsilon E$$

or

$$F = A\varepsilon E$$

We may write expressions for F_c and F_m of the above form as

$$F_c = A_c \varepsilon E_c$$

$$F_m = A_m \varepsilon E_m$$

which, when substituted into the above expression for F_f/F_m, gives

$$\frac{F_f}{F_m} = \frac{A_c \varepsilon E_c}{A_m \varepsilon E_m} - 1$$

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But, $V_m = A_m/A_c$, which, upon rearrangement gives

$$\frac{A_c}{A_m} = \frac{1}{V_m}$$

which, when substituted into the previous expression leads to

$$\frac{F_f}{F_m} = \frac{E_c}{E_m V_m} - 1$$

Also, from Equation 16.10a, $E_c = E_m V_m + E_f V_f$, which, when substituted for E_c into the previous expression, yields

$$\frac{F_f}{F_m} = \frac{E_m V_m + E_f V_f}{E_m V_m} - 1$$

$$= \frac{E_m V_m + E_f V_f - E_m V_m}{E_m V_m} = \frac{E_f V_f}{E_m V_m}$$

the desired result.

(b) This portion of the problem asks that we establish an expression for F_f/F_c. We determine this ratio in a similar manner. Now $F_c = F_f + F_m$ (Equation 16.4), or division by F_c leads to

$$1 = \frac{F_f}{F_c} + \frac{F_m}{F_c}$$

which, upon rearrangement, gives

$$\frac{F_f}{F_c} = 1 - \frac{F_m}{F_c}$$

Now, substitution of the expressions in part (a) for F_m and F_c that resulted from combining Equations 6.1 and 6.5 results in

$$\frac{F_f}{F_c} = 1 - \frac{A_m \varepsilon E_m}{A_c \varepsilon E_c} = 1 - \frac{A_m E_m}{A_c E_c}$$

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Since the volume fraction of fibers is equal to $V_m = A_m/A_c$, then the above equation may be written in the form

$$\frac{F_f}{F_c} = 1 - \frac{V_m E_m}{E_c}$$

And, finally substitution of Equation 16.10(a) for E_c into the above equation leads to the desired result as follows:

$$\frac{F_f}{F_c} = 1 - \frac{V_m E_m}{V_m E_m + V_f E_f}$$

$$= \frac{V_m E_m + V_f E_f - V_m E_m}{V_m E_m + V_f E_f}$$

$$= \frac{V_f E_f}{V_m E_m + V_f E_f}$$

$$= \frac{V_f E_f}{(1 - V_f) E_m + V_f E_f}$$

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16.12 *In an aligned and continuous glass fiber-reinforced nylon 6,6 composite, the fibers are to carry 94% of a load applied in the longitudinal direction.*

(a) Using the data provided, determine the volume fraction of fibers that will be required.

(b) What will be the tensile strength of this composite? Assume that the matrix stress at fiber failure is 30 MPa (4350 psi).

	Modulus of Elasticity **[*GPa* (*psi*)]**	***Tensile Strength*** **[*MPa* (*psi*)]**
Glass fiber	*72.5 (10.5 × 10^6)*	*3400 (490,000)*
Nylon 6,6	*3.0 (4.35 × 10^5)*	*76 (11,000)*

Solution

(a) Given some data for an aligned and continuous glass-fiber-reinforced nylon 6,6 composite, we are asked to compute the volume fraction of fibers that are required such that the fibers carry 94% of a load applied in the longitudinal direction. From Equation 16.11

$$\frac{F_f}{F_m} = \frac{E_f V_f}{E_m V_m} = \frac{E_f V_f}{E_m (1 - V_f)}$$

Now, using values for F_f and F_m from the problem statement

$$\frac{F_f}{F_m} = \frac{0.94}{0.06} = 15.67$$

And when we substitute the given values for E_f and E_m into the first equation leads to

$$\frac{F_f}{F_m} = 15.67 = \frac{(72.5 \text{ GPa}) V_f}{(3.0 \text{ GPa})(1 - V_f)}$$

And, solving for V_f yields, $V_f = 0.393$.

(b) We are now asked for the tensile strength of this composite. From Equation 16.17,

$$\sigma_{cl}^{*} = \sigma_m^{'}(1 - V_f) + \sigma_f^{*} V_f$$

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$$= (30 \text{ MPa})(1 - 0.393) + (3400 \text{ MPa})(0.393)$$

$$= 1354 \text{ MPa} \quad (196{,}400 \text{ psi})$$

since values for σ_f^* (3400 MPa) and σ_m' (30 MPa) are given in the problem statement.

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16.13 *Assume that the composite described in Problem 16.8 has a cross-sectional area of 320 mm^2 (0.50 in.^{2}) and is subjected to a longitudinal load of 44,500 N (10,000 lb$_f$).*

(a) Calculate the fiber–matrix load ratio.

(b) Calculate the actual loads carried by both fiber and matrix phases.

(c) Compute the magnitude of the stress on each of the fiber and matrix phases.

(d) What strain is experienced by the composite?

Solution

The problem stipulates that the cross-sectional area of a composite, A_c, is 320 mm^2 (0.50 in.^{2}), and the longitudinal load, F_c, is 44,500 N (10,000 lb$_f$) for the composite described in Problem 16.8. Also, for this composite

$V_f = 0.3$

$V_m = 0.7$

$E_f = 131$ GPa

$E_m = 2.4$ GPa

(a) First, we are asked to calculate the F_f/F_m ratio. According to Equation 16.11

$$\frac{F_f}{F_m} = \frac{E_f V_f}{E_m V_m} = \frac{(131\ \text{GPa})(0.30)}{(2.4\ \text{GPa})(0.70)} = 23.4$$

Or, $F_f = 23.4F_m$

(b) Now, the actual loads carried by both phases are called for. From Equation 16.4

$$F_f + F_m = F_c = 44{,}500\ \text{N}$$

$$23.4F_m + F_m = 44{,}500\ \text{N}$$

which leads to

$$F_m = 1824\ \text{N}\ \ (410\ \text{lb}_f)$$

$$F_f = F_c - F_m = 44{,}500\ \text{N} - 1824\ \text{N} = 42{,}676\ \text{N}\ \ (9590\ \text{lb}_f)$$

(c) To compute the stress on each of the phases, it is first necessary to know the cross-sectional areas of both fiber and matrix. These are determined as

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$$A_f = V_f A_c = (0.30)(320\ \text{mm}^2) = 96\ \text{mm}^2\ \ (0.15\ \text{in.}^2)$$

$$A_m = V_m A_c = (0.70)(320\ \text{mm}^2) = 224\ \text{mm}^2\ \ (0.35\ \text{in.}^2)$$

Now, the stresses are determined using Equation 6.1 as

$$\sigma_f = \frac{F_f}{A_f} = \frac{42{,}676\ \text{N}}{(96\ \text{mm}^2)(1\ \text{m}/1000\ \text{mm})^2} = 445 \times 10^6\ \text{N/m}^2 = 445\ \text{MPa}\ \ (63{,}930\ \text{psi})$$

$$\sigma_m = \frac{F_m}{A_m} = \frac{1824\ \text{N}}{(224\ \text{mm}^2)(1\ \text{m}/1000\ \text{mm})^2} = 8.14 \times 10^6\ \text{N/m}^2 = 8.14\ \text{MPa}\ \ (1170\ \text{psi})$$

(d) The strain on the composite is the same as the strain on each of the matrix and fiber phases; applying Equation 6.5 to both matrix and fiber phases leads to

$$\varepsilon_m = \frac{\sigma_m}{E_m} = \frac{8.14\ \text{MPa}}{2.4 \times 10^3\ \text{MPa}} = 3.39 \times 10^{-3}$$

$$\varepsilon_f = \frac{\sigma_f}{E_f} = \frac{445\ \text{MPa}}{131 \times 10^3\ \text{MPa}} = 3.39 \times 10^{-3}$$

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16.14 *A continuous and aligned fiber-reinforced composite having a cross-sectional area of 1130 mm^2 (1.75 in.^{2}) is subjected to an external tensile load. If the stresses sustained by the fiber and matrix phases are 156 MPa (22,600 psi) and 2.75 MPa (400 psi), respectively, the force sustained by the fiber phase is 74,000 N (16,600 lb$_f$) and the total longitudinal strain is 1.25 × 10^{-3}, determine*

(a) the force sustained by the matrix phase

(b) the modulus of elasticity of the composite material in the longitudinal direction, and

(c) the moduli of elasticity for fiber and matrix phases.

Solution

(a) For this portion of the problem we are asked to calculate the force sustained by the matrix phase. It is first necessary to compute the volume fraction of the matrix phase, V_m. This may be accomplished by first determining V_f and then V_m from $V_m = 1 - V_f$. The value of V_f may be calculated since, from the definition of stress (Equation 6.1), and realizing $V_f = A_f/A_c$ as

$$\sigma_f = \frac{F_f}{A_f} = \frac{F_f}{V_f A_c}$$

Or, solving for V_f

$$V_f = \frac{F_f}{\sigma_f A_c} = \frac{74{,}000 \text{ N}}{(156 \times 10^6 \text{ N/m}^2)(1130 \text{ mm}^2)(1 \text{ m}/1000 \text{ mm})^2} = 0.420$$

Also

$$V_m = 1 - V_f = 1 - 0.420 = 0.580$$

And, an expression for σ_m analogous to the one for σ_f above is

$$\sigma_m = \frac{F_m}{A_m} = \frac{F_m}{V_m A_c}$$

From which

$$F_m = V_m \sigma_m A_c = (0.580)(2.75 \times 10^6 \text{ N/m}^2)(1.13 \times 10^{-3} \text{ m}^2) = 1802 \text{ N} \quad (406 \text{ lb}_f)$$

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(b) We are now asked to calculate the modulus of elasticity in the longitudinal direction. This is possible realizing that $E_c = \frac{\sigma_c}{\varepsilon}$ (from Equation 6.5) and that $\sigma_c = \frac{F_m + F_f}{A_c}$ (from Equation 6.1). Thus

$$E_c = \frac{\sigma_c}{\varepsilon} = \frac{\frac{F_m + F_f}{A_c}}{\varepsilon} = \frac{F_m + F_f}{\varepsilon A_c}$$

$$= \frac{1802\ \text{N} + 74{,}000\ \text{N}}{(1.25 \times 10^{-3})(1130\ \text{mm}^2)(1\ \text{m}/1000\ \text{mm})^2} = 53.7 \times 10^9\ \text{N/m}^2 = 53.7\ \text{GPa}\quad (7.77 \times 10^6\ \text{psi})$$

(c) Finally, it is necessary to determine the moduli of elasticity for the fiber and matrix phases. This is possible assuming Equation 6.5 for the matrix phase—i.e.,

$$E_m = \frac{\sigma_m}{\varepsilon_m}$$

and, since this is an isostrain state, $\varepsilon_m = \varepsilon_c = 1.25 \times 10^{-3}$. Thus

$$E_m = \frac{\sigma_m}{\varepsilon_c} = \frac{2.75 \times 10^6\ \text{N/m}^2}{1.25 \times 10^{-3}} = 2.2 \times 10^9\ \text{N/m}^2$$

$$= 2.2\ \text{GPa}\quad (3.2 \times 10^5\ \text{psi})$$

The elastic modulus for the fiber phase may be computed in an analogous manner:

$$E_f = \frac{\sigma_f}{\varepsilon_f} = \frac{\sigma_f}{\varepsilon_c} = \frac{156 \times 10^6\ \text{N/m}^2}{1.25 \times 10^{-3}} = 1.248 \times 10^{11}\ \text{N/m}^2$$

$$= 124.8\ \text{GPa}\quad (18.1 \times 10^6\ \text{psi})$$

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16.15 *Compute the longitudinal strength of an aligned carbon fiber-epoxy matrix composite having a 0.25 volume fraction of fibers, assuming the following: (1) an average fiber diameter of* 10×10^{-3} *mm (*3.94×10^{-4} *in.), (2) an average fiber length of 5 mm (0.20 in.), (3) a fiber fracture strength of 2.5 GPa (*3.625×10^{5} *psi), (4) a fiber-matrix bond strength of 80 MPa (11,600 psi), (5) a matrix stress at fiber failure of 10.0 MPa (1450 psi), and (6) a matrix tensile strength of 75 MPa (11,000 psi).*

Solution

It is first necessary to compute the value of the critical fiber length using Equation 16.3. If the fiber length is much greater than l_c, then we may determine the longitudinal strength using Equation 16.17, otherwise, use of either Equation 16.18 or Equation 16.19 is necessary. Thus, from Equation 16.3

$$l_c = \frac{\sigma_f^* d}{2\tau_c} = \frac{(2.5 \times 10^3 \text{ MPa})(10 \times 10^{-3} \text{ mm})}{2(80 \text{ MPa})} = 0.16 \text{ mm}$$

Inasmuch as $l >> l_c$ (5.0 mm >> 0.16 mm), then use of Equation 16.17 is appropriate. Therefore,

$$\sigma_{cl}^* = \sigma_m'(1 - V_f) + \sigma_f^* V_f$$

$$= (10 \text{ MPa})(1 - 0.25) + (2.5 \times 10^3 \text{ MPa})(0.25)$$

$$= 633 \text{ MPa } (91{,}700 \text{ psi})$$

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16.16 *It is desired to produce an aligned carbon fiber-epoxy matrix composite having a longitudinal tensile strength of 750 MPa (109,000 psi). Calculate the volume fraction of fibers necessary if (1) the average fiber diameter and length are 1.2 × 10^{-2} mm (4.7 × 10^{-4} in.) and 1 mm (0.04 in.), respectively; (2) the fiber fracture strength is 5000 MPa (725,000 psi); (3) the fiber-matrix bond strength is 25 MPa (3625 psi); and (4) the matrix stress at fiber failure is 10 MPa (1450 psi).*

Solution

It is first necessary to compute the value of the critical fiber length using Equation 16.3. If the fiber length is much greater than l_c, then we may determine V_f using Equation 16.17, otherwise, use of either Equation 16.18 or Equation 16.19 is necessary. Thus,

$$l_c = \frac{\sigma_f^* d}{2\tau_c} = \frac{(5000\ \text{MPa})(1.2 \times 10^{-2}\ \text{mm})}{2(25\ \text{MPa})} = 1.20\ \text{mm}$$

Inasmuch as $l < l_c$ (1.0 mm < 1.20 mm), then use of Equation 16.19 is required. Therefore,

$$\sigma_{cd'}^* = \frac{l\tau_c}{d} V_f + \sigma_m'(1 - V_f)$$

$$750\,\text{MPa} = \frac{(1.0 \times 10^{-3}\,\text{m})(25\ \text{MPa})}{0.012 \times 10^{-3}\,\text{m}}(V_f) + (10\ \text{MPa})(1 - V_f)$$

Solving this expression for V_f leads to V_f = 0.357.

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16.17 *Compute the longitudinal tensile strength of an aligned glass fiber-epoxy matrix composite in which the average fiber diameter and length are 0.010 mm (4×10^{-4} in.) and 2.5 mm (0.10 in.), respectively, and the volume fraction of fibers is 0.40. Assume that (1) the fiber-matrix bond strength is 75 MPa (10,900 psi), (2) the fracture strength of the fibers is 3500 MPa (508,000 psi), and (3) the matrix stress at fiber failure is 8.0 MPa (1160 psi).*

Solution

It is first necessary to compute the value of the critical fiber length using Equation 16.3. If the fiber length is much greater than l_c, then we may determine σ_{cl}^* using Equation 16.17, otherwise, use of either Equations 16.18 or 16.19 is necessary. Thus,

$$l_c = \frac{\sigma_f^* d}{2\tau_c} = \frac{(3500 \text{ MPa})(0.010 \text{ mm})}{2(75 \text{ MPa})} = 0.233 \text{ mm} \quad (0.0093 \text{ in.})$$

Inasmuch as $l > l_c$ (2.5 mm > 0.233 mm), but since l is not much greater than l_c, then use of Equation 16.18 is necessary. Therefore,

$$\sigma_{cd}^* = \sigma_f^* V_f \left(1 - \frac{l_c}{2l}\right) + \sigma_m' (1 - V_f)$$

$$= (3500 \text{ MPa})(0.40)\left[1 - \frac{0.233 \text{ mm}}{(2)(2.5 \text{ mm})}\right] + (8.0 \text{ MPa})(1 - 0.40)$$

$$= 1340 \text{ MPa} \quad (194{,}400 \text{ psi})$$

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16.18 *(a) From the moduli of elasticity data in Table 16.2 for glass fiber-reinforced polycarbonate composites, determine the value of the fiber efficiency parameter for each of 20, 30, and 40 vol% fibers.*

(b) Estimate the modulus of elasticity for 50 vol% glass fibers.

Solution

(a) This portion of the problem calls for computation of values of the fiber efficiency parameter. From Equation 16.20

$$E_{cd} = KE_f V_f + E_m V_m$$

Solving this expression for K yields

$$K = \frac{E_{cd} - E_m V_m}{E_f V_f} = \frac{E_{cd} - E_m(1 - V_f)}{E_f V_f}$$

For glass fibers, $E_f = 72.5$ GPa (Table 16.4); using the data in Table 16.2, and taking an average of the extreme E_m values given, $E_m = 2.29$ GPa (0.333×10^6 psi). And, for $V_f = 0.20$

$$K = \frac{5.93\ \text{GPa} - (2.29\ \text{GPa})(1 - 0.2)}{(72.5\ \text{GPa})(0.2)} = 0.283$$

For $V_f = 0.3$

$$K = \frac{8.62\ \text{GPa} - (2.29\ \text{GPa})(1 - 0.3)}{(72.5\ \text{GPa})(0.3)} = 0.323$$

And, for $V_f = 0.4$

$$K = \frac{11.6\ \text{GPa} - (2.29\ \text{GPa})(1 - 0.4)}{(72.5\ \text{GPa})(0.4)} = 0.353$$

(b) For 50 vol% fibers ($V_f = 0.50$), we must assume a value for K. Since it is increasing with V_f, let us estimate it to increase by the same amount as going from 0.3 to 0.4—that is, by a value of 0.03. Therefore, let us assume a value for K of 0.383. Now, from Equation 16.20

$$E_{cd} = KE_f V_f + E_m V_m$$

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$$= (0.383)(72.5\ \text{GPa})(0.5) + (2.29\ \text{GPa})(0.5)$$

$$= 15.0\ \text{GPa}\ \ (2.18 \times 10^6\ \text{psi})$$

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The Fiber Phase
The Matrix Phase

16.19 *For a polymer-matrix fiber-reinforced composite,*

(a) List three functions of the matrix phase.

(b) Compare the desired mechanical characteristics of matrix and fiber phases.

(c) Cite two reasons why there must be a strong bond between fiber and matrix at their interface.

Solution

(a) For polymer-matrix fiber-reinforced composites, three functions of the polymer-matrix phase are: (1) to bind the fibers together so that the applied stress is distributed among the fibers; (2) to protect the surface of the fibers from being damaged; and (3) to separate the fibers and inhibit crack propagation.

(b) The matrix phase must be ductile and is usually relatively soft, whereas the fiber phase must be stiff and strong.

(c) There must be a strong interfacial bond between fiber and matrix in order to: (1) maximize the stress transmittance between matrix and fiber phases; and (2) minimize fiber pull-out, and the probability of failure.

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16.20 *(a) What is the distinction between matrix and dispersed phases in a composite material?*

(b) Contrast the mechanical characteristics of matrix and dispersed phases for fiber-reinforced composites.

Solution

(a) The matrix phase is a continuous phase that surrounds the noncontinuous dispersed phase.

(b) In general, the matrix phase is relatively weak, has a low elastic modulus, but is quite ductile. On the other hand, the fiber phase is normally quite strong, stiff, and brittle.

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Polymer-Matrix Composites

16.21 *(a) Calculate and compare the specific longitudinal strengths of the glass-fiber, carbon-fiber, and aramid-fiber reinforced epoxy composites in Table 16.5 with the following alloys: tempered (315°C) 440A martensitic stainless steel, normalized 1020 plain-carbon steel, 2024-T3 aluminum alloy, cold-worked (HO2 temper) C36000 free-cutting brass, rolled AZ31B magnesium alloy, and annealed Ti-6Al-4V titanium alloy.*

(b) Compare the specific moduli of the same three fiber-reinforced epoxy composites with the same metal alloys. Densities (i.e., specific gravities), tensile strengths, and moduli of elasticity for these metal alloys may be found in Tables B.1, B.4, and B.2, respectively, in Appendix B.

Solution

(a) This portion of the problem calls for us to calculate the specific longitudinal strengths of glass-fiber, carbon-fiber, and aramid-fiber reinforced epoxy composites, and then to compare these values with the specific strengths of several metal alloys.

The longitudinal specific strength of the glass-reinforced epoxy material ($V_f = 0.60$) in Table 16.5 is just the ratio of the longitudinal tensile strength and specific gravity as

$$\frac{1020 \text{ MPa}}{2.1} = 486 \text{ MPa}$$

For the carbon-fiber reinforced epoxy

$$\frac{1240 \text{ MPa}}{1.6} = 775 \text{ MPa}$$

And, for the aramid-fiber reinforced epoxy

$$\frac{1380 \text{ MPa}}{1.4} = 986 \text{ MPa}$$

Now, for the metal alloys we use data found in Tables B.1 and B.4 in Appendix B (using the density values from Table B.1 for the specific gravities). For the 440A tempered martensitic steel

$$\frac{1790 \text{ MPa}}{7.80} = 229 \text{ MPa}$$

For the normalized 1020 plain carbon steel, the ratio is

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$$\frac{440\ \text{MPa}}{7.85} = 56\ \text{MPa}$$

For the 2024-T3 aluminum alloy

$$\frac{485\ \text{MPa}}{2.77} = 175\ \text{MPa}$$

For the C36000 brass (cold worked)

$$\frac{400\ \text{MPa}}{8.50} = 47\ \text{MPa}$$

For the AZ31B (rolled) magnesium alloy

$$\frac{290\ \text{MPa}}{1.77} = 164\ \text{MPa}$$

For the annealed Ti-6Al-4V titanium alloy

$$\frac{900\ \text{MPa}}{4.43} = 203\ \text{MPa}$$

(b) The longitudinal specific modulus is just the longitudinal tensile modulus-specific gravity ratio. For the glass-fiber reinforced epoxy, this ratio is

$$\frac{45\ \text{GPa}}{2.1} = 21.4\ \text{GPa}$$

For the carbon-fiber reinforced epoxy

$$\frac{145\ \text{GPa}}{1.6} = 90.6\ \text{GPa}$$

And, for the aramid-fiber reinforced epoxy

$$\frac{76\ \text{GPa}}{1.4} = 54.3\ \text{GPa}$$

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The specific moduli for the metal alloys (Tables B.1 and B.2) are as follows:

For the 440A tempered martensitic steel

$$\frac{200\ \text{GPa}}{7.80} = 25.6\ \text{GPa}$$

For the normalized 1020 plain-carbon steel

$$\frac{207\ \text{GPa}}{7.85} = 26.4\ \text{GPa}$$

For the 2024-T3 aluminum alloy

$$\frac{72.4\ \text{GPa}}{2.77} = 26.1\ \text{GPa}$$

For the cold-worked C36000 brass

$$\frac{97\ \text{GPa}}{8.50} = 11.4\ \text{GPa}$$

For the rolled AZ31B magnesium alloy

$$\frac{45\ \text{GPa}}{1.77} = 25.4\ \text{GPa}$$

For the Ti-6Al-4V titanium alloy

$$\frac{114\ \text{GPa}}{4.43} = 25.7\ \text{GPa}$$

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16.22 *(a) List four reasons why glass fibers are most commonly used for reinforcement.*

(b) Why is the surface perfection of glass fibers so important?

(c) What measures are taken to protect the surface of glass fibers?

Solution

(a) The four reasons why glass fibers are most commonly used for reinforcement are listed at the beginning of Section 16.8 under "Glass Fiber-Reinforced Polymer (GFRP) Composites."

(b) The surface perfection of glass fibers is important because surface flaws or cracks act as points of stress concentration, which will dramatically reduce the tensile strength of the material.

(c) Care must be taken not to rub or abrade the surface after the fibers are drawn. As a surface protection, newly drawn fibers are coated with a protective surface film.

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16.23 *Cite the distinction between carbon and graphite.*

Solution

"Graphite" is crystalline carbon having the structure shown in Figure 12.17, whereas "carbon" will consist of some noncrystalline material as well as areas of crystal misalignment.

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16.24 *(a) Cite several reasons why fiberglass-reinforced composites are utilized extensively.*

(b) Cite several limitations of this type of composite.

Solution

(a) Reasons why fiberglass-reinforced composites are utilized extensively are: (1) glass fibers are very inexpensive to produce; (2) these composites have relatively high specific strengths; and (3) they are chemically inert in a wide variety of environments.

(b) Several limitations of these composites are: (1) care must be exercised in handling the fibers inasmuch as they are susceptible to surface damage; (2) they are lacking in stiffness in comparison to other fibrous composites; and (3) they are limited as to maximum temperature use.

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Hybrid Composites

16.25 *(a) What is a hybrid composite?*

(b) List two important advantages of hybrid composites over normal fiber composites.

Solution

(a) A hybrid composite is a composite that is reinforced with two or more different fiber materials in a single matrix.

(b) Two advantages of hybrid composites are: (1) better overall property combinations, and (2) failure is not as catastrophic as with single-fiber composites.

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16.26 *(a) Write an expression for the modulus of elasticity for a hybrid composite in which all fibers of both types are oriented in the same direction.*

(b) Using this expression, compute the longitudinal modulus of elasticity of a hybrid composite consisting of aramid and glass fibers in volume fractions of 0.30 and 0.40, respectively, within a polyester resin matrix [E_m = 2.5 GPa (3.6×10^5 psi)].

Solution

(a) For a hybrid composite having all fibers aligned in the same direction

$$E_{cl} = E_m V_m + E_{f1} V_{f1} + E_{f2} V_{f2}$$

in which the subscripts *f*1 and *f*2 refer to the two types of fibers.

(b) Now we are asked to compute the longitudinal elastic modulus for a glass- and aramid-fiber hybrid composite. From Table 16.4, the elastic moduli of aramid and glass fibers are, respectively, 131 GPa (19×10^6 psi) and 72.5 GPa (10.5×10^6 psi). Thus, from the previous expression

$$E_{cl} = (2.5 \text{ GPa})(1.0 - 0.30 - 0.40) + (131 \text{ GPa})(0.30) + (72.5 \text{ GPa})(0.40)$$

$$= 69.1 \text{ GPa} \quad (10.0 \times 10^6 \text{ psi})$$

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16.27 *Derive a generalized expression analogous to Equation 16.16 for the transverse modulus of elasticity of an aligned hybrid composite consisting of two types of continuous fibers.*

Solution

This problem asks that we derive a generalized expression analogous to Equation 16.16 for the transverse modulus of elasticity of an aligned hybrid composite consisting of two types of continuous fibers. Let us denote the subscripts *f*1 and *f*2 for the two fiber types, and *m* , *c*, and *t* subscripts for the matrix, composite, and transverse direction, respectively. For the isostress state, the expressions analogous to Equations 16.12 and 16.13 are

$$\sigma_c = \sigma_m = \sigma_{f1} = \sigma_{f2}$$

And

$$\varepsilon_c = \varepsilon_m V_m + \varepsilon_{f1} V_{f1} + \varepsilon_{f2} V_{f2}$$

Since $\varepsilon = \sigma/E$ (Equation 6.5), making substitutions of the form of this equation into the previous expression yields

$$\frac{\sigma}{E_{ct}} = \frac{\sigma}{E_m} V_m + \frac{\sigma}{E_{f1}} V_{f1} + \frac{\sigma}{E_{f2}} V_{f2}$$

Thus

$$\frac{1}{E_{ct}} = \frac{V_m}{E_m} + \frac{V_{f1}}{E_{f1}} + \frac{V_{f2}}{E_{f2}}$$

$$= \frac{V_m E_{f1} E_{f2} + V_{f1} E_m E_{f2} + V_{f2} E_m E_{f1}}{E_m E_{f1} E_{f2}}$$

And, finally, taking the reciprocal of this equation leads to

$$E_{ct} = \frac{E_m E_{f1} E_{f2}}{V_m E_{f1} E_{f2} + V_{f1} E_m E_{f2} + V_{f2} E_m E_{f1}}$$

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Processing of Fiber-Reinforced Composites

16.28 *Briefly describe pultrusion, filament winding, and prepreg production fabrication processes; cite the advantages and disadvantages of each.*

Solution

Pultrusion, filament winding, and prepreg fabrication processes are described in Section 16.13.

For pultrusion, the advantages are: the process may be automated, production rates are relatively high, a wide variety of shapes having constant cross-sections are possible, and very long pieces may be produced. The chief disadvantage is that shapes are limited to those having a constant cross-section.

For filament winding, the advantages are: the process may be automated, a variety of winding patterns are possible, and a high degree of control over winding uniformity and orientation is afforded. The chief disadvantage is that the variety of shapes is somewhat limited.

For prepreg production, the advantages are: resin does not need to be added to the prepreg, the lay-up arrangement relative to the orientation of individual plies is variable, and the lay-up process may be automated. The chief disadvantages of this technique are that final curing is necessary after fabrication, and thermoset prepregs must be stored at subambient temperatures to prevent complete curing.

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Laminar Composites
Sandwich Panels

16.29 *Briefly describe laminar composites. What is the prime reason for fabricating these materials?*

Solution

Laminar composites are a series of sheets or panels, each of which has a preferred high-strength direction. These sheets are stacked and then cemented together such that the orientation of the high-strength direction varies from layer to layer.

These composites are constructed in order to have a relatively high strength in virtually all directions within the plane of the laminate.

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16.30 *(a) Briefly describe sandwich panels.*

(b) What is the prime reason for fabricating these structural composites?

(c) What are the functions of the faces and the core?

Solution

(a) Sandwich panels consist of two outer face sheets of a high-strength material that are separated by a layer of a less-dense and lower-strength core material.

(b) The prime reason for fabricating these composites is to produce structures having high in-plane strengths, high shear rigidities, and low densities.

(c) The faces function so as to bear the majority of in-plane tensile and compressive stresses. On the other hand, the core separates and provides continuous support for the faces, and also resists shear deformations perpendicular to the faces.

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DESIGN PROBLEMS

16.D1 *Composite materials are now being utilized extensively in sports equipment.*

(a) List at least four different sports implements that are made of, or contain composites.

(b) For one of these implements, write an essay in which you do the following: (1) Cite the materials that are used for matrix and dispersed phases, and, if possible, the proportions of each phase; (2) note the nature of the dispersed phase (i.e., continuous fibers); and (3) describe the process by which the implement is fabricated.

Solution

Inasmuch as there are a number of different sports implements that employ composite materials, no attempt will be made to provide a complete answer for this question. However, a list of this type of sporting equipment would include skis and ski poles, fishing rods, vaulting poles, golf clubs, hockey sticks, baseball and softball bats, surfboards and boats, oars and paddles, bicycle components (frames, wheels, handlebars), canoes, and tennis and racquetball rackets.

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Influence of Fiber Orientation and Concentration

16.D2 *It is desired to produce an aligned and continuous fiber-reinforced epoxy composite having a maximum of 50 vol% fibers. In addition, a minimum longitudinal modulus of elasticity of 50 GPa (7.3 × 10^6 psi) is required, as well as a minimum tensile strength of 1300 MPa (189,000 psi). Of E-glass, carbon (PAN standard modulus), and aramid fiber materials, which are possible candidates and why? The epoxy has a modulus of elasticity of 3.1 GPa (4.5 × 10^5 psi) and a tensile strength of 75 MPa (11,000 psi). In addition, assume the following stress levels on the epoxy matrix at fiber failure: E-glass—70 MPa (10,000 psi); carbon (PAN standard modulus)—30 MPa (4350 psi); and aramid—50 MPa (7250 psi). Other fiber data are contained in Tables B.2 and B.4 in Appendix B. For aramid and carbon fibers, use average strengths computed from the minimum and maximum values provided in Table B.4.*

Solution

In order to solve this problem, we want to make longitudinal elastic modulus and tensile strength computations assuming 50 vol% fibers for all three fiber materials, in order to see which meet the stipulated criteria [i.e., a minimum elastic modulus of 50 GPa (7.3 × 10^6 psi), and a minimum tensile strength of 1300 MPa (189,000 psi)]. Thus, it becomes necessary to use Equations 16.10b and 16.17 with $V_m = 0.5$ and $V_f = 0.5$, $E_m = 3.1$ GPa, and $\sigma_m^* = 75$ MPa.

For glass, $E_f = 72.5$ GPa and $\sigma_f^* = 3450$ MPa. Therefore,

$$E_{cl} = E_m(1 - V_f) + E_f V_f$$

$$= (3.1\text{ GPa})(1 - 0.5) + (72.5\text{ GPa})(0.5) = 37.8\text{ GPa} \quad (5.48 \times 10^6\text{ psi})$$

Since this is less than the specified minimum (i.e., 50 GPa), glass is not an acceptable candidate.

For carbon (PAN standard-modulus), $E_f = 230$ GPa and $\sigma_f^* = 4000$ MPa (the average of the range of values in Table B.4), thus, from Equation 16.10b

$$E_{cl} = (3.1\text{ GPa})(0.5) + (230\text{ GPa})(0.5) = 116.6\text{ GPa} \quad (16.9 \times 10^6\text{ psi})$$

which is greater than the specified minimum. In addition, from Equation 16.17

$$\sigma_{cl}^* = \sigma_m^{\prime}(1 - V_f) + \sigma_f^* V_f$$

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$$= (30 \text{ MPa})(0.5) + (4000 \text{ MPa})(0.5) = 2015 \text{ MPa} \quad (292,200 \text{ psi})$$

which is also greater than the minimum (1300 MPa). Thus, carbon (PAN standard-modulus) is a candidate.

For aramid, $E_f = 131$ GPa and $\sigma_f^* = 3850$ MPa (the average of the range of values in Table B.4), thus (Equation 16.10b)

$$E_{cl} = (3.1 \text{ GPa})(0.5) + (131 \text{ GPa})(0.5) = 67.1 \text{ GPa} \quad (9.73 \times 10^6 \text{ psi})$$

which value is greater than the minimum. In addition, from Equation 16.17

$$\sigma_{cl}^* = \sigma_m'(1 - V_f) + \sigma_f^* V_f$$

$$= (50 \text{ MPa})(0.5) + (3850 \text{ MPa})(0.5) = 1950 \text{ MPa} \quad (283,600 \text{ psi})$$

which is also greater than the minimum strength value. Therefore, of the three fiber materials, both the carbon (PAN standard-modulus) and the aramid meet both minimum criteria.

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16.D3 *It is desired to produce a continuous and oriented carbon fiber-reinforced epoxy having a modulus of elasticity of at least 83 GPa (12×10^6 psi) in the direction of fiber alignment. The maximum permissible specific gravity is 1.40. Given the following data, is such a composite possible? Why or why not? Assume that composite specific gravity may be determined using a relationship similar to Equation 16.10a.*

	SpecificGravity	***Modulus of Elasticity* [*GPa* (*psi*)]**
Carbon fiber	*1.80*	*260 (37×10^6)*
Epoxy	*1.25*	*2.4 (3.5×10^5)*

Solution

This problem asks us to determine whether or not it is possible to produce a continuous and oriented carbon fiber-reinforced epoxy having a modulus of elasticity of at least 83 GPa in the direction of fiber alignment, and a maximum specific gravity of 1.40. We will first calculate the minimum volume fraction of fibers to give the stipulated elastic modulus, and then the maximum volume fraction of fibers possible to yield the maximum permissible specific gravity; if there is an overlap of these two fiber volume fractions then such a composite is possible.

With regard to the elastic modulus, from Equation 16.10b

$$E_{cl} = E_m(1 - V_f) + E_f V_f$$

$$83 \text{ GPa} = (2.4 \text{ GPa})(1 - V_f) + (260 \text{ GPa})(V_f)$$

Solving for V_f yields $V_f = 0.31$. Therefore, $V_f > 0.31$ to give the minimum desired elastic modulus.

Now, upon consideration of the specific gravity (or density), ρ, we employ the following modified form of Equation 16.10b

$$\rho_c = \rho_m(1 - V_f) + \rho_f V_f$$

$$1.40 = 1.25(1 - V_f) + 1.80(V_f)$$

And, solving for V_f from this expression gives $V_f = 0.27$. Therefore, it is necessary for $V_f < 0.27$ in order to have a composite specific gravity less than 1.40.

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Hence, such a composite is *not possible* since there is no overlap of the fiber volume fractions as computed using the two stipulated criteria.

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16.D4 *It is desired to fabricate a continuous and aligned glass fiber-reinforced polyester having a tensile strength of at least 1400 MPa (200,000 psi) in the longitudinal direction. The maximum possible specific gravity is 1.65. Using the following data, determine if such a composite is possible. Justify your decision. Assume a value of 15 MPa for the stress on the matrix at fiber failure.*

	Specific Gravity	***Tensile Strength* [*MPa* (*psi*)]**
Glass fiber	2.50	3500 (5×10^5)
Polyester	1.35	50 (7.25×10^3)

Solution

This problem asks us to determine whether or not it is possible to produce a continuous and oriented glass fiber-reinforced polyester having a tensile strength of at least 1400 MPa in the longitudinal direction, and a maximum specific gravity of 1.65. We will first calculate the minimum volume fraction of fibers to give the stipulated tensile strength, and then the maximum volume fraction of fibers possible to yield the maximum permissible specific gravity; if there is an overlap of these two fiber volume fractions then such a composite is possible.

With regard to tensile strength, from Equation 16.17

$$\sigma_{cl}^{*} = \sigma_{m}^{'}(1 - V_f) + \sigma_{f}^{*}V_f$$

$$1400 \text{ MPa} = (15 \text{ MPa})(1 - V_f) + (3500 \text{ MPa})(V_f)$$

Solving for V_f yields $V_f = 0.397$. Therefore, $V_f > 0.397$ to give the minimum desired tensile strength.

Now, upon consideration of the specific gravity (or density), ρ, we employ the following modified form of Equation 16.10b:

$$\rho_c = \rho_m(1 - V_f) + \rho_f V_f$$

$$1.65 = 1.35(1 - V_f) + 2.50(V_f)$$

And, solving for V_f from this expression gives $V_f = 0.261$. Therefore, it is necessary for $V_f < 0.261$ in order to have a composite specific gravity less than 1.65.

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Hence, such a composite is *not possible* since there is no overlap of the fiber volume fractions as computed using the two stipulated criteria.

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16.D5 *It is necessary to fabricate an aligned and discontinuous carbon fiber-epoxy matrix composite having a longitudinal tensile strength of 1900 MPa (275,000 psi) using 0.45 volume fraction of fibers. Compute the required fiber fracture strength assuming that the average fiber diameter and length are 8×10^{-3} mm (3.1×10^{-4} in.) and 3.5 mm (0.14 in.), respectively. The fiber-matrix bond strength is 40 MPa (5800 psi), and the matrix stress at fiber failure is 12 MPa (1740 psi).*

Solution

In this problem, for an aligned and discontinuous carbon fiber-epoxy matrix composite having a longitudinal tensile strength of 1900 MPa, we are asked to compute the required fiber fracture strength, given the following: the average fiber diameter (8.0×10^{-3} mm), the average fiber length (3.5 mm), the volume fraction of fibers (0.45), the fiber-matrix bond strength (40 MPa), and the matrix stress at fiber failure (12 MPa).

To begin, since the value of σ_f^* is unknown, calculation of the value of l_c in Equation 16.3 is not possible, and, therefore, we are not able to decide which of Equations 16.18 and 16.19 to use. Thus, it is necessary to substitute for l_c in Equation 16.3 into Equation 16.18, solve for the value of σ_f^*, then, using this value, solve for l_c from Equation 16.3. If $l > l_c$, we use Equation 16.18, otherwise Equation 16.19 must be used. *Note:* the σ_f^* parameters in Equations 16.18 and 16.3 are the same. Realizing this, and substituting for l_c in Equation 16.3 into Equation 16.18 leads to

$$\sigma_{cd}^* = \sigma_f^* V_f \left[1 - \frac{l_c}{2l}\right] + \sigma_m'(1 - V_f) = \sigma_f^* V_f \left[1 - \frac{\sigma_f^* d}{4\tau_c l}\right] + \sigma_m'(1 - V_f)$$

$$= \sigma_f^* V_f - \frac{\sigma_f^{*2} V_f d}{4\tau_c l} + \sigma_m' - \sigma_m' V_f$$

This expression is a quadratic equation in which σ_f^* is the unknown. Rearrangement into a more convenient form leads to

$$\sigma_f^{*2}\left[\frac{V_f d}{4\tau_c l}\right] - \sigma_f^*(V_f) + \left[\sigma_{cd}^* - \sigma_m'(1 - V_f)\right] = 0$$

Or

$$a\sigma_f^{*2} + b\sigma_f^* + c = 0$$

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where

$$a = \frac{V_f d}{4\tau_c l}$$

$$= \frac{(0.45)(8 \times 10^{-6}\ \text{m})}{(4)(40\ \text{MPa})(3.5 \times 10^{-3}\ \text{m})} = 6.43 \times 10^{-6}\ (\text{MPa})^{-1} \quad \left[4.29 \times 10^{-8}\ (\text{psi})^{-1}\right]$$

Furthermore,

$$b = -V_f = -0.45$$

And

$$c = \sigma_{cd}^{*} - \sigma_m'(1 - V_f)$$

$$= 1900\ \text{MPa} - (12\ \text{MPa})(1 - 0.45) = 1893.4\ \text{MPa} \quad (274{,}043\ \text{psi})$$

Now solving the above quadratic equation for σ_f^* yields

$$\sigma_f^* = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-(-0.45) \pm \sqrt{(-0.45)^2 - (4)\left[6.43 \times 10^{-6}\ (\text{MPa})^{-1}\right](1893.4\ \text{MPa})}}{(2)\left[6.43 \times 10^{-6}\ (\text{MPa})^{-1}\right]}$$

$$= \frac{0.4500 \pm 0.3922}{1.286 \times 10^{-5}}\ \text{MPa} \quad \left[\frac{0.4500 \pm 0.3943}{8.58 \times 10^{-8}}\ \text{psi}\right]$$

This yields the two possible roots as

$$\sigma_f^*(+) = \frac{0.4500 + 0.3922}{1.286 \times 10^{-5}}\ \text{MPa} = 65{,}500\ \text{MPa} \quad (9.84 \times 10^{6}\ \text{psi})$$

$$\sigma_f^*(-) = \frac{0.4500 - 0.3922}{1.286 \times 10^{-5}}\ \text{MPa} = 4495\ \text{MPa} \quad (650{,}000\ \text{psi})$$

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Upon consultation of the magnitudes of σ_f^* for various fibers and whiskers in Table 16.4, only $\sigma_f^*(-)$ is reasonable. Now, using this value, let us calculate the value of l_c using Equation 16.3 in order to ascertain if use of Equation 16.18 in the previous treatment was appropriate. Thus

$$l_c = \frac{\sigma_f^* d}{2\tau_c} = \frac{(4495 \text{ MPa})(0.008 \text{ mm})}{(2)(40 \text{ MPa})} = 0.45 \text{ mm} \quad (0.0173 \text{ in.})$$

Since $l > l_c$ (3.5 mm > 0.45 mm), our choice of Equation 16.18 was indeed appropriate, and σ_f^* = 4495 MPa (650,000 psi).

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16.D6 *A tubular shaft similar to that shown in Figure 16.11 is to be designed that has an outside diameter of 80 mm (3.15 in.) and a length of 0.75 m (2.46 ft). The mechanical characteristic of prime importance is bending stiffness in terms of the longitudinal modulus of elasticity. Stiffness is to be specified as maximum allowable deflection in bending; when subjected to three-point bending as in Figure 12.32, a load of 1000 N (225 lb_f) is to produce an elastic deflection of no more than 0.40 mm (0.016 in.) at the midpoint position.*

Continuous fibers that are oriented parallel to the tube axis will be used; possible fiber materials are glass, and carbon in standard-, intermediate-, and high-modulus grades. The matrix material is to be an epoxy resin, and fiber volume fraction is 0.35.

(a) Decide which of the four fiber materials are possible candidates for this application, and for each candidate determine the required inside diameter consistent with the above criteria.

(b) For each candidate, determine the required cost, and on this basis, specify the fiber that would be the least expensive to use.

Elastic modulus, density, and cost data for the fiber and matrix materials are contained in Table 16.6.

Solution

(a) This portion of the problem calls for a determination of which of the four fiber types is suitable for a tubular shaft, given that the fibers are to be continuous and oriented with a volume fraction of 0.35. Using Equation 16.10 it is possible to solve for the elastic modulus of the shaft for each of the fiber types. For example, for glass (using moduli data in Table 16.6)

$$E_{cs} = E_m(1 - V_f) + E_f V_f$$

$$= (2.4\ \text{GPa})(1.00 - 0.35) + (72.5\ \text{GPa})(0.35) = 26.9\ \text{GPa}$$

This value for E_{cs} as well as those computed in a like manner for the three carbon fibers are listed in Table 16.D1.

Table 16.D1 Composite Elastic Modulus for Each of Glass and Three Carbon Fiber Types for V_f= 0.35

Fiber Type	E_{cs} (GPa)
Glass	26.9
Carbon—standard modulus	82.1
Carbon—intermediate modulus	101.3
Carbon—high modulus	141.6

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It now becomes necessary to determine, for each fiber type, the inside diameter d_i. Rearrangement of Equation 16.23 such that d_i is the dependent variable leads to

$$d_i = \left[d_0^4 - \frac{4FL^3}{3\pi E \Delta y} \right]^{1/4}$$

The d_i values may be computed by substitution into this expression for E the E_{cs} data in Table 16.D1 and the following

$F = 1000$ N

$L = 0.75$ m

$\Delta y = 0.4$ mm

$d_0 = 80$ mm

These d_i data are tabulated in the first column of Table 16.D2. Thus, all four materials are candidates for this application, and the inside diameter for each material is given in the first column of this table.

Table 16.D2 Inside Tube Diameter, Total Volume, and Fiber, Matrix, and Total Costs for Three Carbon-Fiber Epoxy-Matrix Composites

Fiber Type	Inside Diameter (mm)	Total Volume (cm^3)	Fiber Cost ($)	Matrix Cost ($)	Total Cost ($)
Glass	70.2	867	1.64	3.86	5.50
Carbon--standard modulus	77.2	259	9.79	1.15	10.94
Carbon--intermediate modulus	77.7	214	12.81	0.95	13.76
Carbon--high modulus	78.4	149	23.47	0.66	24.13

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(b) Also included in Table 16.D2 is the total volume of material required for the tubular shaft for each fiber type; Equation 16.24 was utilized for these computations. Since $V_f = 0.35$, 35% this volume is fiber and the other 65% is epoxy matrix. In the manner of Design Example 16.1, the masses and costs of fiber and matrix materials were determined, as well as the total composite cost. These data are also included in Table 16.D2. Here it may be noted that the glass fiber yields the least expensive composite, followed by the standard-, intermediate-, and high-modulus carbon fiber materials.

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CHAPTER 17

CORROSION AND DEGRADATION OF MATERIALS

PROBLEM SOLUTIONS

Electrochemical Considerations

17.1 *(a) Briefly explain the difference between oxidation and reduction electrochemical reactions.*

(b) Which reaction occurs at the anode and which at the cathode?

Solution

(a) Oxidation is the process by which an atom gives up an electron (or electrons) to become a cation. Reduction is the process by which an atom acquires an extra electron (or electrons) and becomes an anion.

(b) Oxidation occurs at the anode; reduction at the cathode.

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17.2 *(a) Write the possible oxidation and reduction half-reactions that occur when magnesium is immersed in each of the following solutions: (i) HCl, (ii) an HCl solution containing dissolved oxygen, (iii) an HCl solution containing dissolved oxygen and, in addition, Fe^{2+} ions.*

(b) In which of these solutions would you expect the magnesium to oxidize most rapidly? Why?

Solution

(a) This problem asks that we write possible oxidation and reduction half-reactions for magnesium in various solutions.

(i) In HCl, possible reactions are

$$Mg \rightarrow Mg^{2+} + 2e^- \quad \text{(oxidation)}$$

$$2H^+ + 2e^- \rightarrow H_2 \quad \text{(reduction)}$$

(ii) In an HCl solution containing dissolved oxygen, possible reactions are

$$Mg \rightarrow Mg^{2+} + 2e^- \quad \text{(oxidation)}$$

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \quad \text{(reduction)}$$

(iii) In an HCl solution containing dissolved oxygen and Fe^{2+} ions, possible reactions are

$$Mg \rightarrow Mg^{2+} + 2e^- \quad \text{(oxidation)}$$

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \quad \text{(reduction)}$$

$$Fe^{2+} + 2e^- \rightarrow Fe \quad \text{(reduction)}$$

(b) The magnesium would probably oxidize most rapidly in the HCl solution containing dissolved oxygen and Fe^{2+} ions because there are two reduction reactions that will consume electrons from the oxidation of magnesium.

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17.3 *Demonstrate that (a) the value of $\mathscr{F}$ in Equation 17.19 is 96,500 C/mol, and (b) at 25°C (298 K),*

$$\frac{RT}{nF}\ln x = \frac{0.0592}{n}\log x$$

Solution

(a) The Faraday constant $\mathscr{F}$ (represented here as "F") is just the product of the charge per electron and Avogadro's number; that is

$$F = eN_A = (1.602 \times 10^{-19}\ \text{C/electron})(6.022 \times 10^{23}\ \text{electrons/mol})$$

$$= 96{,}472\ \text{C/mol}$$

(b) At 25°C (298 K),

$$\frac{RT}{nF}\ln(x) = \frac{(8.31\ \text{J/mol-K})(298\ \text{K})}{(n)(96{,}472\ \text{C/mol})}(2.303)\log(x)$$

$$= \frac{0.0592}{n}\log(x)$$

This gives units in volts since a volt is a J/C.

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17.4 *(a) Compute the voltage at 25°C of an electrochemical cell consisting of pure cadmium immersed in a* 2×10^{-3} *M solution of* Cd^{2+} *ions, and pure iron in a 0.4 M solution of* Fe^{2+} *ions.*

(b) Write the spontaneous electrochemical reaction.

Solution

(a) We are asked to compute the voltage of a nonstandard Cd-Fe electrochemical cell. Since iron is lower in the emf series (Table 17.1), we will begin by assuming that iron is oxidized and cadmium is reduced, as

$$Fe + Cd^{2+} \rightarrow Fe^{2+} + Cd$$

and Equation 17.20 takes the form

$$\Delta V = (V^{\square}_{Cd} - V^{\square}_{Fe}) - \frac{0.0592}{2} \log \frac{[Fe^{2+}]}{[Cd^{2+}]}$$

$$= [-0.403 \text{ V} - (-0.440 \text{ V})] - \frac{0.0592}{2} \log \left[\frac{0.40}{2 \times 10^{-3}} \right]$$

$$= -0.031 \text{ V}$$

since, from Table 17.1, the standard potentials for Cd and Fe are –0.403 and –0.440, respectively.

(b) Since the ΔV is negative, the spontaneous cell direction is just the reverse of that above, or

$$Fe^{2+} + Cd \rightarrow Fe + Cd^{2+}$$

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17.5 *A Zn/Zn^{2+} concentration cell is constructed in which both electrodes are pure zinc. The Zn^{2+} concentration for one cell half is 1.0 M , for the other, 10^{-2} M . Is a voltage generated between the two cell halves? If so, what is its magnitude and which electrode will be oxidized? If no voltage is produced, explain this result.*

Solution

This problem calls for us to determine whether or not a voltage is generated in a Zn/Zn^{2+} concentration cell, and, if so, its magnitude. Let us label the Zn cell having a 1.0 *M* Zn^{2+} solution as cell 1, and the other as cell 2. Furthermore, assume that oxidation occurs within cell 2, wherein $[Zn_2^{2+}] = 10^{-2}$ *M*. Hence,

$$Zn_2 + Zn_1^{2+} \rightarrow Zn_2^{2+} + Zn_1$$

and, employing Equation 17.20 leads to

$$\Delta V = -\frac{0.0592}{2} \log \frac{\left[Zn_2^{2+}\right]}{\left[Zn_1^{2+}\right]}$$

$$= -\frac{0.0592}{2} \log \left[\frac{10^{-2}\,M}{1.0\,M}\right] = +0.0592 \text{ V}$$

Therefore, a voltage of 0.0592 V is generated when oxidation occurs in the cell having the Zn^{2+} concentration of 10^{-2} *M*.

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17.6 *An electrochemical cell is composed of pure copper and pure lead electrodes immersed in solutions of their respective divalent ions. For a 0.6 M concentration of Cu^{2+}, the lead electrode is oxidized yielding a cell potential of 0.507 V. Calculate the concentration of Pb^{2+} ions if the temperature is 25°C.*

Solution

We are asked to calculate the concentration of Pb^{2+} ions in a copper-lead electrochemical cell. The electrochemical reaction that occurs within this cell is just

$$Pb + Cu^{2+} \rightarrow Pb^{2+} + Cu$$

while $\Delta V = 0.507$ V and $[Cu^{2+}] = 0.6\ M$. Thus, Equation 17.20 is written in the form

$$\Delta V = \left(V^{\square}_{Cu} - V^{\square}_{Pb}\right) - \frac{0.0592}{2} \log \frac{[Pb^{2+}]}{[Cu^{2+}]}$$

This equation may be rewritten as

$$-\frac{\Delta V - \left(V^{\square}_{Cu} - V^{\square}_{Pb}\right)}{0.0296} = \log \frac{[Pb^{2+}]}{[Cu^{2+}]}$$

Solving this expression for $[Pb^{2+}]$ gives

$$[Pb^{2+}] = [Cu^{2+}] \exp\left[(2.303)\frac{\Delta V - \left(V^{\square}_{Cu} - V^{\square}_{Pb}\right)}{0.0296}\right]$$

The standard potentials from Table 17.1 are $V^{\square}_{Cu} = +0.340$ V and $V^{\square}_{Pb} = -0.126$ V. Therefore,

$$[Pb^{2+}] = (0.6\ M) \exp\left[(2.303)\frac{0.507\ \text{V} - \{0.340\ \text{V} - (-0.126\ \text{V})\}}{0.0296}\right]$$

$$= 2.5 \times 10^{-2}\ M$$

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17.7 *An electrochemical cell is constructed such that on one side a pure nickel electrode is in contact with a solution containing Ni^{2+} ions at a concentration of 3×10^{-3} M. The other cell half consists of a pure Fe electrode that is immersed in a solution of Fe^{2+} ions having a concentration of 0.1 M. At what temperature will the potential between the two electrodes be +0.140 V?*

Solution

This problem asks for us to calculate the temperature for a nickel-iron electrochemical cell when the potential between the Ni and Fe electrodes is +0.140 V. On the basis of their relative positions in the standard emf series (Table 17.1), assume that Fe is oxidized and Ni is reduced. Thus, the electrochemical reaction that occurs within this cell is just

$$Ni^{2+} + Fe \rightarrow Ni + Fe^{2+}$$

Thus, Equation 17.20 is written in the form

$$\Delta V = \left(V^{\square}_{Ni} - V^{\square}_{Fe}\right) - \frac{RT}{nF} \ln \frac{[Fe^{2+}]}{[Ni^{2+}]}$$

Solving this expression for T gives

$$T = -\frac{nF}{R}\left[\frac{\Delta V - \left(V^{\square}_{Ni} - V^{\square}_{Fe}\right)}{\ln \dfrac{[Fe^{2+}]}{[Ni^{2+}]}}\right]$$

The standard potentials from Table 17.1 are $V^{\square}_{Fe} = -0.440$ V and $V^{\square}_{Ni} = -0.250$ V. Therefore,

$$T = -\frac{(2)(96{,}500\ \text{C/mol})}{8.31\ \text{J/mol-K}}\left[\frac{0.140\ \text{V} - \{-0.250\ \text{V} - (-0.440\ \text{V})\}}{\ln\left(\dfrac{0.1\ M}{3 \times 10^{-3}\ M}\right)}\right]$$

$$= 331\ \text{K} = 58°\text{C}$$

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17.8 *For the following pairs of alloys that are coupled in seawater, predict the possibility of corrosion; if corrosion is probable, note which metal/alloy will corrode.*

(a) Aluminum and magnesium

(b) Zinc and a low-carbon steel

(c) Brass (60Cu–40Zn) and Monel (70Ni–30Cu)

(d) Titanium and 304 stainless steel

(e) Cast iron and 316 stainless steel

Solution

This problem asks, for several pairs of alloys that are immersed in seawater, to predict whether or not corrosion is possible, and if it is possible, to note which alloy will corrode. In order to make these predictions it is necessary to use the galvanic series, Table 17.2. If both of the alloys in the pair reside within the same set of brackets in this table, then galvanic corrosion is unlikely. However, if the two alloys do not lie within the same set of brackets, then that alloy appearing lower in the table will experience corrosion.

(a) For the aluminum-magnesium couple, corrosion is possible, and magnesium will corrode.

(b) For the zinc-low carbon steel couple, corrosion is possible, and zinc will corrode.

(c) For the brass-monel couple, corrosion is unlikely inasmuch as both alloys appear within the same set of brackets.

(d) For the titanium-304 stainless steel pair, the stainless steel will corrode, inasmuch as it is below titanium in both its active and passive states.

(e) For the cast iron-316 stainless steel couple, the cast iron will corrode since it is below stainless steel in both active and passive states.

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17.9 *(a) From the galvanic series (Table 17.2), cite three metals or alloys that may be used to galvanically protect 304 stainless steel in the active state.*

(b) As Concept Check 17.4(b) notes, galvanic corrosion is prevented by making an electrical contact between the two metals in the couple and a third metal that is anodic to the other two. Using the galvanic series, name one metal that could be used to protect a copper–aluminum galvanic couple.

Solution

(a) The following metals and alloys may be used to galvanically protect 304 stainless steel in the active state: cast iron, iron/steels, aluminum/aluminum alloys, cadmium, zinc, magnesium/magnesium alloys. These metals/alloys appear below cast iron in the galvanic series. Table 17.2.

(b) Zinc and magnesium may be used to protect a copper-aluminum galvanic couple; these metals are anodic to aluminum in the galvanic series.

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Corrosion Rates

17.10 *Demonstrate that the constant K in Equation 17.23 will have values of 534 and 87.6 for the CPR in units of mpy and mm/yr, respectively.*

Solution

This problem is just an exercise in unit conversions. The parameter K in Equation 17.23 must convert the units of W, ρ, A, and t, into the unit scheme for the CPR.

For CPR in mpy (mil/yr)

$$K = \frac{W(\text{mg})(1\ \text{g}/1000\ \text{mg})}{\rho\left(\frac{\text{g}}{\text{cm}^3}\right)\left(\frac{2.54\ \text{cm}}{\text{in.}}\right)^3\left[A(\text{in.}^2)\right]\left(\frac{1\ \text{in.}}{1000\ \text{mil}}\right)[t(\text{h})]\left(\frac{1\ \text{day}}{24\ \text{h}}\right)\left(\frac{1\ \text{yr}}{365\ \text{days}}\right)}$$

$$= 534.6$$

For CPR in mm/yr

$$K = \frac{W(\text{mg})(1\ \text{g}/1000\ \text{mg})}{\rho\left(\frac{\text{g}}{\text{cm}^3}\right)\left(\frac{1\ \text{cm}}{10\ \text{mm}}\right)^3\left[A(\text{cm}^2)\right]\left(\frac{10\ \text{mm}}{\text{cm}}\right)^2[t(\text{h})]\left(\frac{1\ \text{day}}{24\ \text{h}}\right)\left(\frac{1\ \text{yr}}{365\ \text{days}}\right)}$$

$$= 87.6$$

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17.11 *A piece of corroded steel plate was found in a submerged ocean vessel. It was estimated that the original area of the plate was 10 in.^{2} and that approximately 2.6 kg had corroded away during the submersion. Assuming a corrosion penetration rate of 200 mpy for this alloy in seawater, estimate the time of submersion in years. The density of steel is 7.9 g/cm^3.*

Solution

This problem calls for us to compute the time of submersion of a steel plate. In order to solve this problem, we must first rearrange Equation 17.23, as

$$t = \frac{KW}{\rho A\,(\text{CPR})}$$

Thus, using values for the various parameters given in the problem statement

$$t = \frac{(534)\left(2.6 \times 10^6 \text{ mg}\right)}{\left(7.9 \text{ g/cm}^3\right)\left(10 \text{ in.}^2\right)(200 \text{ mpy})}$$

$$= 8.8 \times 10^4 \text{ h} = 10 \text{ yr}$$

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17.12 *A thick steel sheet of area 400 cm^2 is exposed to air near the ocean. After a one-year period it was found to experience a weight loss of 375 g due to corrosion. To what rate of corrosion, in both mpy and mm/yr, does this correspond?*

Solution

This problem asks for us to calculate the CPR in both mpy and mm/yr for a thick steel sheet of area 400 cm^2 which experiences a weight loss of 375 g after one year. Employment of Equation 17.23 leads to

$$\text{CPR(mm/yr)} = \frac{KW}{\rho A t}$$

$$= \frac{(87.6)(375\ \text{g})(10^3\ \text{mg/g})}{(7.9\ \text{g/cm}^3)(400\ \text{cm}^2)(24\ \text{h/day})(365\ \text{day/yr})(1\ \text{yr})}$$

$$= 1.2\ \text{mm/yr}$$

Also

$$\text{CPR(mpy)} = \frac{(534)(375\ \text{g})(10^3\ \text{mg/g})}{(7.9\ \text{g/cm}^3)(400\ \text{in.}^2)(1\ \text{in./2.54 cm})^2(24\ \text{h/day})(365\ \text{day/yr})(1\ \text{yr})}$$

$$= 46.7\ \text{mpy}$$

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17.13 *(a) Demonstrate that the CPR is related to the corrosion current density i (A/cm^2) through the expression*

$$\text{CPR} = \frac{KA\,i}{n\rho} \qquad (17.38)$$

where K is a constant, A is the atomic weight of the metal experiencing corrosion, n is the number of electrons associated with the ionization of each metal atom, and ρ is the density of the metal.

(b) Calculate the value of the constant K for the CPR in mpy and i in $\mu A/cm^2$ (10^{-6} A/cm^2).

Solution

(a) We are to demonstrate that the CPR is related to the corrosion current density, *i*, in A/cm^2 through the expression

$$\text{CPR} = \frac{KA\,i}{n\rho}$$

in which *K* is a constant, *A* is the atomic weight, *n* is the number of electrons ionized per metal atom, and ρ is the density of the metal. Possibly the best way to make this demonstration is by using a unit dimensional analysis. The corrosion rate, *r*, in Equation 17.24 has the units (SI)

$$r = \frac{i}{nF} = \frac{\text{C/m}^2\text{-s}}{(\text{unitless})(\text{C/mol})} = \frac{\text{mol}}{\text{m}^2\text{-s}}$$

The units of CPR in Equation 17.23 are length/time, or in the SI scheme, m/s. In order to convert the above expression to the units of m/s it is necessary to multiply *r* by the atomic weight *A* and divide by the density ρ as

$$\frac{rA}{\rho} = \frac{(\text{mol/m}^2\text{-s})(\text{g/mol})}{\text{g/m}^3} = \text{m/s}$$

Thus, the CPR is proportional to *r*, and substituting for *r* from Equation 17.24 into the above expression leads to

$$\text{CPR} = K''r = \frac{K'\,A\,i}{nF\rho}$$

in which *K′* and *K″* are constants which will give the appropriate units for CPR. Also, since *F* (i.e., Faraday's constant) is also a constant, this expression will take the form

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$$\text{CPR} = \frac{KA\,i}{n\rho}$$

in which $K = K'/F$.

(b) Now we will calculate the value of K in order to give the CPR in mpy for i in $\mu A/cm^2$ (10^{-6} A/cm^2). It should be noted that the units of A (in $\mu A/cm^2$) are amperes or C/s. Substitution of the units normally used into the former CPR expression above leads to

$$\text{CPR} = K'\frac{A\,i}{nF\rho}$$

$$= K'\ \frac{(\text{g/mol})(\text{C/s-cm}^2)}{(\text{unitless})(\text{C/mol})(\text{g/cm}^3)} = \text{cm/s}$$

Since we want the CPR in mpy and i is given in $\mu A/cm^2$, and realizing that $K = K'/F$ leads to

$$K = \left(\frac{1}{96{,}500\ \text{C/mol}}\right)\left(\frac{10^{-6}\ \text{C}}{\mu\text{C}}\right)\left(\frac{1\ \text{in.}}{2.54\ \text{cm}}\right)\left(\frac{10^3\ \text{mil}}{\text{in.}}\right)\left(\frac{3.1536\ \times 10^7\ \text{s}}{\text{yr}}\right)$$

$$= 0.129$$

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17.14 *Using the results of Problem 17.13, compute the corrosion penetration rate, in mpy, for the corrosion of iron in citric acid (to form Fe^{2+} ions) if the corrosion current density is 1.15×10^{-5} A/cm^2.*

Solution

We are asked to compute the CPR in mpy for the corrosion of Fe for a corrosion current density of 1.15×10^{-5} A/cm^2 (11.5 μA/cm^2). From Problem 17.13, the value of K in Equation 17.38 is 0.129, and therefore

$$\text{CPR} = \frac{KAi}{n\rho}$$

$$= \frac{(0.129)(55.85 \text{ g/mol})(11.5 \text{ μA/cm}^2)}{(2)(7.9 \text{ g/cm}^3)} = 5.24 \text{ mpy}$$

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Prediction of Corrosion Rates

17.15 *(a) Cite the major differences between activation and concentration polarizations.*

(b) Under what conditions is activation polarization rate controlling?

(c) Under what conditions is concentration polarization rate controlling?

Solution

(a) Activation polarization is the condition wherein a reaction rate is controlled by one step in a series of steps that takes place at the slowest rate. For corrosion, activation polarization is possible for both oxidation and reduction reactions. Concentration polarization occurs when a reaction rate is limited by diffusion in a solution. For corrosion, concentration polarization is possible only for reduction reactions.

(b) Activation polarization is rate controlling when the reaction rate is low and/or the concentration of active species in the liquid solution is high.

(c) Concentration polarization is rate controlling when the reaction rate is high and/or the concentration of active species in the liquid solution is low.

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17.16 *(a) Describe the phenomenon of dynamic equilibrium as it applies to oxidation and reduction electrochemical reactions.*

(b) What is the exchange current density?

Solution

(a) The phenomenon of dynamic equilibrium is the state wherein oxidation and reduction reactions are occurring at the same rate such that there is no net observable reaction.

(b) The exchange current density is just the current density which is related to both the rates of oxidation and reduction (which are equal) according to Equation 17.26 for the dynamic equilibrium state.

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17.17 *Lead experiences corrosion in an acid solution according to the reaction*

$$Pb + 2H^+ \rightarrow Pb^{2+} + H_2$$

The rates of both oxidation and reduction half-reactions are controlled by activation polarization.

(a) Compute the rate of oxidation of Pb (in mol/cm^2-s) given the following activation polarization data:

For Lead	***For Hydrogen***
$V_{(Pb/Pb^{2+})} = -0.126$ V	$V_{(H^+/H_2)} = 0$ V
$i_0 = 2 \times 10^{-9}$ A/cm^2	$i_0 = 1.0 \times 10^{-8}$ A/cm^2
$\beta = +0.12$	$\beta = -0.10$

(b) Compute the value of the corrosion potential.

Solution

(a) This portion of the problem asks that we compute the rate of oxidation for Pb given that both the oxidation and reduction reactions are controlled by activation polarization, and also given the polarization data for both lead oxidation and hydrogen reduction. The first thing necessary is to establish relationships of the form of Equation 17.25 for the potentials of both oxidation and reduction reactions. Next we will set these expressions equal to one another, and then solve for the value of i which is really the corrosion current density, i_c. Finally, the corrosion rate may be calculated using Equation 17.24. The two potential expressions are as follows:

For hydrogen reduction

$$V_H = V_{(H^+/H_2)} + \beta_H \log\left(\frac{i}{i_{0_H}}\right)$$

And for Pb oxidation

$$V_{Pb} = V_{(Pb/Pb^{2+})} + \beta_{Pb} \log\left(\frac{i}{i_{0_{Pb}}}\right)$$

Setting $V_H = V_{Pb}$ and solving for log i (log i_c) leads to

$$\log i_c = \left(\frac{1}{\beta_{Pb} - \beta_H}\right)\left[V_{(H^+/H_2)} - V_{(Pb/Pb^{2+})} - \beta_H \log i_{0_H} + \beta_{Pb} \log i_{0_{Pb}}\right]$$

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And, incorporating values for the various parameters provided in the problem statement leads to

$$\log i_c = \left[\frac{1}{0.12 - (-0.10)}\right]\left[0 - (-0.126) - (-0.10)\left\{\log\left(1.0 \times 10^{-8}\right)\right\} + (0.12)\left\{\log\left(2 \times 10^{-9}\right)\right\}\right]$$

$$= -7.809$$

Or

$$i_c = 10^{-7.809} = 1.55 \times 10^{-8}\ \text{A/cm}^2$$

And from Equation 17.24

$$r = \frac{i_c}{nF}$$

$$= \frac{1.55 \times 10^{-8}\ \text{C/s-cm}^2}{(2)(96{,}500\ \text{C/mol})} = 8.03 \times 10^{-14}\ \text{mol/cm}^2\text{-s}$$

(b) Now it becomes necessary to compute the value of the corrosion potential, V_c. This is possible by using either of the above equations for V_H or V_{Pb} and substituting for i the value determined above for i_c. Thus

$$V_c = V_{(H^+/H_2)} + \beta_H \log\left(\frac{i_c}{i_{0_H}}\right)$$

$$= 0 + (-0.10\ \text{V})\log\left(\frac{1.55 \times 10^{-8}\ \text{A/cm}^2}{1.0 \times 10^{-8}\ \text{A/cm}^2}\right) = -0.019\ \text{V}$$

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17.18 *The corrosion rate is to be determined for some divalent metal M in a solution containing hydrogen ions. The following corrosion data are known about the metal and solution:*

For Metal M	***For Hydrogen***
$V_{(M/M^{2+})} = -0.47$ V	$V_{(H^+/H_2)} = 0$ V
$i_0 = 5 \times 10^{-10}$ A/cm^2	$i_0 = 2 \times 10^{-9}$ A/cm^2
$\beta = +0.15$	$\beta = -0.12$

(a) Assuming that activation polarization controls both oxidation and reduction reactions, determine the rate of corrosion of metal M (in mol/cm^2-s).

(b) Compute the corrosion potential for this reaction.

Solution

(a) This portion of the problem asks that we compute the rate of oxidation for a divalent metal M given that both the oxidation and reduction reactions are controlled by activation polarization, and also given the polarization data for both M oxidation and hydrogen reduction. The first thing necessary is to establish relationships of the form of Equation 17.25 for the potentials of both oxidation and reduction reactions. Next we will set these expressions equal to one another, and then solve for the value of i which is really the corrosion current density, i_c. Finally, the corrosion rate may be calculated using Equation 17.24. The two potential expressions are as follows:

For hydrogen reduction

$$V_H = V_{(H^+/H_2)} + \beta_H \log\left(\frac{i}{i_{0_H}}\right)$$

And for M oxidation

$$V_M = V_{(M/M^{2+})} + \beta_M \log\left(\frac{i}{i_{0_M}}\right)$$

Setting $V_H = V_M$ and solving for log i (log i_c) leads to

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$$\log i_c = \left(\frac{1}{\beta_M - \beta_H}\right)\left[V_{(H^+/H_2)} - V_{(M/M^{2+})} - \beta_H \log i_{0_H} + \beta_M \log i_{0_M}\right]$$

And, incorporating values for the various parameters provided in the problem statement leads to

$$\log i_c = \left[\frac{1}{0.15 - (-0.12)}\right]\left[0 - (-0.47) - (-0.12)\left\{\log\left(2 \times 10^{-9}\right)\right\} + (0.15)\left\{\log\left(5 \times 10^{-10}\right)\right\}\right]$$

$$= -7.293$$

Or

$$i_c = 10^{-7.293} = 5.09 \times 10^{-8}\ \text{A/cm}^2$$

And from Equation 17.24

$$r = \frac{i_c}{nF}$$

$$= \frac{5.09 \times 10^{-8}\ \text{C/s-cm}^2}{(2)(96{,}500\ \text{C/mol})} = 2.64 \times 10^{-13}\ \text{mol/cm}^2\text{-s}$$

(b) Now it becomes necessary to compute the value of the corrosion potential, V_c. This is possible by using either of the above equations for V_H or V_M and substituting for i the value determined above for i_c. Thus

$$V_c = V_{(H^+/H_2)} + \beta_H \log\left(\frac{i_c}{i_{0_H}}\right)$$

$$= 0 + (-0.12\ \text{V}) \log\left(\frac{5.09 \times 10^{-8}\ \text{A/cm}^2}{2 \times 10^{-9}\ \text{A/cm}^2}\right) = -0.169\ \text{V}$$

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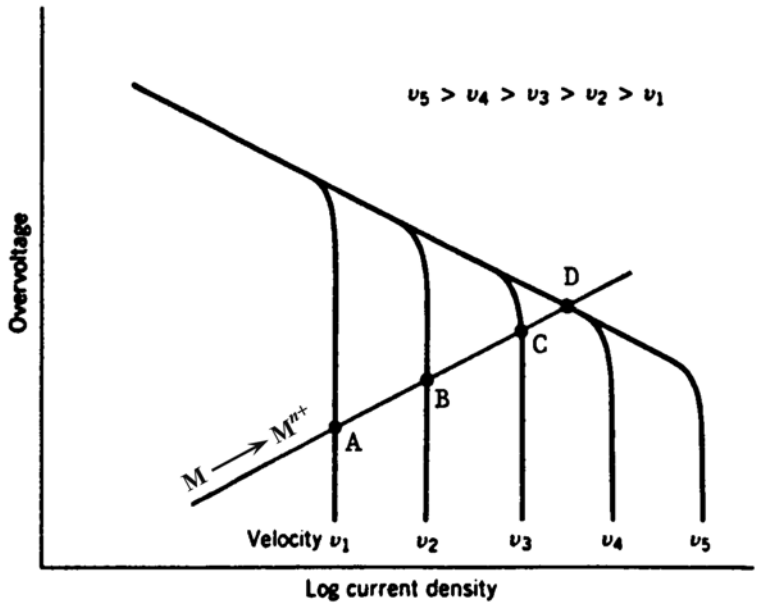
17.19 *The influence of increasing solution velocity on the overvoltage-versus-log current density behavior for a solution that experiences combined activation–concentration polarization is indicated in Figure 17.26. On the basis of this behavior, make a schematic plot of corrosion rate versus solution velocity for the oxidation of a metal; assume that the oxidation reaction is controlled by activation polarization.*

Solution

This problem asks that we make a schematic plot of corrosion rate versus solution velocity. The reduction reaction is controlled by combined activation-concentration polarization for which the overvoltage versus logarithm current density is presented in Figure 17.26. The oxidation of the metal is controlled by activation polarization, such that the electrode kinetic behavior for the combined reactions would appear schematically as shown below.



Thus, the plot of corrosion rate versus solution velocity would be as

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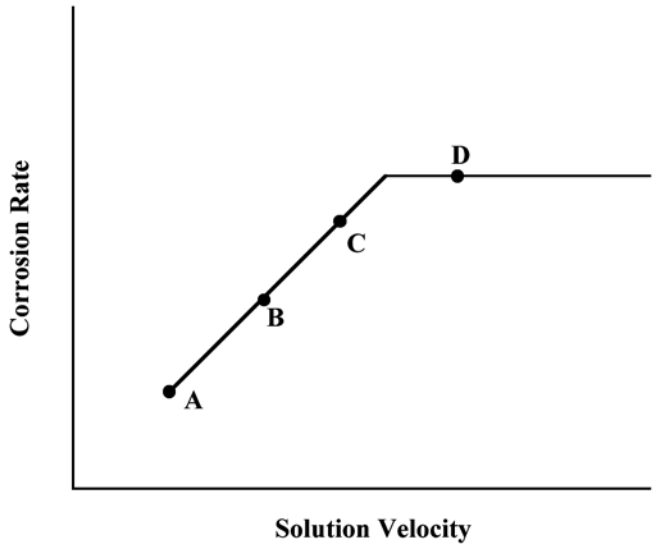

The corrosion rate initially increases with increasing solution velocity (for velocities v_1, v_2, and v_3), corresponding to intersections in the concentration polarization regions for the reduction reaction. However, for the higher solution velocities (v_4 and v_5), the metal oxidation line intersects the reduction reaction curve in the linear activation polarization region, and, thus, the reaction becomes independent of solution velocity.

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Passivity

17.20 *Briefly describe the phenomenon of passivity. Name two common types of alloy that passivate.*

Solution

Passivity is the loss of chemical reactivity, under particular environmental conditions, of normally active metals and alloys. Stainless steels and aluminum alloys often passivate.

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17.21 *Why does chromium in stainless steels make them more corrosion resistant in many environments than plain carbon steels?*

Solution

The chromium in stainless steels causes a very thin and highly adherent surface coating to form over the surface of the alloy, which protects it from further corrosion. For plain carbon steels, rust, instead of this adherent coating, forms.

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Forms of Corrosion

17.22 *For each form of corrosion, other than uniform, do the following:*

(a) Describe why, where, and the conditions under which the corrosion occurs.

(b) Cite three measures that may be taken to prevent or control it.

For each of the forms of corrosion, the conditions under which it occurs, and measures that may be taken to prevent or control it are outlined in Section 17.7.

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17.23 *Briefly explain why cold-worked metals are more susceptible to corrosion than noncold-worked metals.*

Solution

Cold-worked metals are more susceptible to corrosion than noncold-worked metals because of the increased dislocation density for the latter. The region in the vicinity of a dislocation that intersects the surface is at a higher energy state, and, therefore, is more readily attacked by a corrosive solution.

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17.24 *Briefly explain why, for a small anode-to-cathode area ratio, the corrosion rate will be higher than for a large ratio.*

Solution

For a small anode-to-cathode area ratio, the corrosion rate will be higher than for a large ratio. The reason for this is that for some given current flow associated with the corrosion reaction, for a small area ratio the current density at the anode will be greater than for a large ratio. The corrosion rate is proportional to the current density (i) according to Equation 17.24.

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17.25 *For a concentration cell, briefly explain why corrosion occurs at that region having the lower concentration.*

Solution

For a concentration cell, corrosion occurs at that region having the lower concentration. In order to explain this phenomenon let us consider an electrochemical cell consisting of two divalent metal M electrodes each of which is immersed in a solution containing a different concentration of its M^{2+} ion; let us designate the low and high concentrations of M^{2+} as $[M_L^{2+}]$ and $[M_H^{2+}]$, respectively. Now assuming that reduction and oxidation reactions occur in the high- and low-concentration solutions, respectively, let us determine the cell potential in terms of the two $[M^{2+}]$'s; if this potential is positive then we have chosen the solutions in which the reduction and oxidation reactions appropriately.

Thus, the two half-reactions in the form of Equations 17.16 are

$$M_H^{2+} + 2e^- \rightarrow M \qquad V_M^{\square}$$

$$M \rightarrow M_L^{2+} + 2e^- \qquad V_M^{\square}$$

Whereas the overall cell reaction is

$$M_H^{2+} + M \rightarrow M + M_L^{2+}$$

From Equation 17.19, this yields a cell potential of

$$\Delta V = V_M^{\square} - V_M^{\square} - \frac{RT}{nF} \ln \left(\frac{[M_L^{2+}]}{[M_H^{2+}]} \right)$$

$$= - \frac{RT}{nF} \ln \left(\frac{[M_L^{2+}]}{[M_H^{2+}]} \right)$$

Inasmuch as $[M_L^{2+}] < [M_H^{2+}]$ then the natural logarithm of the $[M^{2+}]$ ratio is negative, which yields a positive value for ΔV. This means that the electrochemical reaction is spontaneous as written, or that oxidation occurs at the electrode having the lower M^{2+} concentration.

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Corrosion Prevention

17.26 *(a) What are inhibitors?*

(b) What possible mechanisms account for their effectiveness?

Solution

(a) Inhibitors are substances that, when added to a corrosive environment in relatively low concentrations, decrease the environment's corrosiveness.

(b) Possible mechanisms that account for the effectiveness of inhibitors are: (1) elimination of a chemically active species in the solution; (2) attachment of inhibitor molecules to the corroding surface so as to interfere with either the oxidation or reduction reaction; and (3) the formation of a very thin and protective coating on the corroding surface.

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17.27 *Briefly describe the two techniques that are used for galvanic protection.*

Solution

Descriptions of the two techniques used for galvanic protection are as follows:

(1) A sacrificial anode is electrically coupled to the metal piece to be protected, which anode is also situated in the corrosion environment. The sacrificial anode is a metal or alloy that is chemically more reactive in the particular environment. It (the anode) preferentially oxidizes, and, upon giving up electrons to the other metal, protects it from electrochemical corrosion.

(2) An impressed current from an external dc power source provides excess electrons to the metallic structure to be protected.

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Oxidation

17.28 *For each of the metals listed in the table, compute the Pilling–Bedworth ratio. Also, on the basis of this value, specify whether or not you would expect the oxide scale that forms on the surface to be protective, and then justify your decision. Density data for both the metal and its oxide are also tabulated.*

Metal	***Metal Density*** ***(g/cm^3)***	***Metal Oxide***	***Oxide Density*** ***(g/cm^3)***
Zr	*6.51*	ZrO_2	*5.89*
Sn	*7.30*	SnO_2	*6.95*
Bi	*9.80*	Bi_2O_3	*8.90*

Solution

With this problem we are given, for three metals, their densities, oxide chemical formulas, and oxide densities, and are asked to compute the Pilling-Bedworth ratios, and then to specify whether or not the oxide scales that form will be protective. The general form of the equation used to calculate this ratio is Equation 17.32 (or Equation 17.33). For zirconium, oxidation occurs by the reaction

$$Zr + O_2 \rightarrow ZrO_2$$

and therefore, from Equation 17.32

$$\text{P} - \text{B ratio} = \frac{A_{ZrO_2}\rho_{Zr}}{A_{Zr}\rho_{ZrO_2}}$$

$$= \frac{(123.22\ \text{g/mol})(6.51\ \text{g/cm}^3)}{(91.22\ \text{g/mol})(5.89\ \text{g/cm}^3)} = 1.49$$

Thus, this would probably be a protective oxide film since the P-B ratio lies between one and two.

The oxidation reaction for Sn is just

$$Sn + O_2 \rightarrow SnO_2$$

and the P-B ratio is (Equation 17.32)

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$$\text{P} - \text{B ratio} = \frac{A_{SnO_2}\rho_{Sn}}{A_{Sn}\rho_{SnO_2}}$$

$$= \frac{(150.71\ \text{g/mol})(7.30\ \text{g/cm}^3)}{(118.71\ \text{g/mol})(6.95\ \text{g/cm}^3)} = 1.33$$

Hence, the film would most likely be protective since the ratio lies between one and two.

Now for Bi, the reaction for its oxidation is

$$2\text{Bi} + \frac{3}{2}\text{O}_2 \rightarrow \text{Bi}_2\text{O}_3$$

and the P-B ratio is (Equation 17.33)

$$\text{P} - \text{B ratio} = \frac{A_{Bi_2O_3}\rho_{Bi}}{(2)A_{Bi}\rho_{Bi_2O_3}}$$

$$= \frac{(465.96\ \text{g/mol})(9.80\ \text{g/cm}^3)}{(2)(208.98\ \text{g/mol})(8.90\ \text{g/cm}^3)} = 1.23$$

Thus, the Bi_2O_3 film would probably be protective since the ratio is between one and two.

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17.29 *According to Table 17.3, the oxide coating that forms on silver should be nonprotective, and yet Ag does not oxidize appreciably at room temperature and in air. How do you explain this apparent discrepancy?*

Solution

Silver does not oxidize appreciably at room temperature and in air even though, according to Table 17.3, the oxide coating should be nonprotective. The reason for this is that the oxidation of silver in air is not thermodynamically favorable; therefore, the lack of a reaction is independent of whether or not a protective scale forms.

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17.30 *In the table, weight gain-time data for the oxidation of copper at an elevated temperature are tabulated.*

***W* (*mg/cm*^{2})**	***Time* (*min*)**
0.316	*15*
0.524	*50*
0.725	*100*

(a) Determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression.

(b) Now compute W after a time of 450 min.

Solution

For this problem we are given weight gain-time data for the oxidation of Cu at an elevated temperature.

(a) We are first asked to determine whether the oxidation kinetics obey a parabolic, linear, or logarithmic rate expression, which expressions are represented by Equations 17.34, 17.35, and 17.36, respectively. One way to make this determination is by trial and error. Let us assume that the parabolic relationship is valid; that is from Equation 17.34

$$W^2 = K_1 t + K_2$$

which means that we may establish three simultaneous equations using the three sets of given W and t values, then using two combinations of two pairs of equations, solve for K_1 and K_2; if K_1 and K_2 have the same values for both solutions, then the kinetics are parabolic. If the values are not identical then the other kinetic relationships need to be explored. Thus, the three equations are

$$(0.316)^2 = 0.100 = 15K_1 + K_2$$
$$(0.524)^2 = 0.275 = 50K_1 + K_2$$
$$(0.725)^2 = 0.526 = 100K_1 + K_2$$

From the first two equations $K_1 = 5 \times 10^{-3}$ and $K_2 = 0.025$; these same two values are obtained using the last two equations. Hence, the oxidation rate law is parabolic.

(b) Since a parabolic relationship is valid, this portion of the problem calls for us to determine W after a total time of 450 min. Again, using Equation 17.34 and the values of K_1 and K_2

$$W^2 = K_1 t + K_2$$

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$$= (5 \times 10^{-3})(450 \text{ min}) + 0.025 = 2.28$$

Or $W = \sqrt{2.28} = 1.51$ mg/cm^2.

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17.31 *In the table, weight gain–time data for the oxidation of some metal at an elevated temperature are tabulated.*

***W* (*mg/cm*^{2})**	***Time* (*min*)**
4.66	*20*
11.7	*50*
41.1	*135*

(a) Determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression.

(b) Now compute W after a time of 1000 min.

Solution

For this problem we are given weight gain-time data for the oxidation of some metal at an elevated temperature.

(a) We are first asked to determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression, which expressions are described by Equations 17.35, 17.34, and 17.36, respectively. One way to make this determination is by trial and error. Let us assume that the rate expression is linear, that is from Equation 17.35

$$W = K_3 t$$

which means that we may establish three simultaneous equations using the three sets of given W and t values, then solve for K_3 for each; if K_3 is the same for all three cases, then the rate law is linear. If the values are not the same then the other kinetic relationships need to be explored. Thus, the three equations are

$$4.66 = 20K_3$$
$$11.7 = 50K_3$$
$$41.1 = 175K_3$$

In all three instances the value of K_3 is about equal to 0.234, which means the oxidation rate obeys a linear expression.

(b) Now we are to calculate W after a time of 1000 min; thus

$$W = K_3 t = (0.234)(1000 \text{ min}) = 234 \text{ mg/cm}^2$$

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17.32 *In the table, weight gain–time data for the oxidation of some metal at an elevated temperature are tabulated.*

***W* (*mg/cm*^{2})**	***Time* (*min*)**
1.90	*25*
3.76	*75*
6.40	*250*

(a) Determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression.

(b) Now compute W after a time of 3500 min.

Solution

For this problem we are given weight gain-time data for the oxidation of some metal at an elevated temperature.

(a) We are first asked to determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression, which expressions are described by Equations 17.35, 17.34, and 17.36, respectively. One way to make this determination is by trial and error. Let us assume that the kinetic rate is parabolic, that is from Equation 17.34

$$W^2 = K_1 t + K_2$$

which means that we may establish three simultaneous equations using the three sets of given W and t values, then using two combinations of two pairs of equations, solve for K_1 and K_2; if K_1 and K_2 have the same values for both solutions, then the weight gain-time relationships are parabolic. If the values are not the same then the other kinetic relationships need to be explored. Thus, the three equations are

$$(1.90)^2 = 3.610 = 25K_1 + K_2$$
$$(3.67)^2 = 13.47 = 75K_1 + K_2$$
$$(6.40)^2 = 40.96 = 250K_1 + K_2$$

From the first two equations $K_1 = 0.197$ and $K_2 = -1.32$; while from the second and third equations $K_1 = 0.157$ and $K_2 = 1.689$. Thus, a parabolic rate expression is not obeyed by this reaction.

Let us now investigate linear kinetics in the same manner, using Equation 17.35, $W = K_3 t$. The three equations are thus

$$1.90 = 25K_3$$
$$3.67 = 75K_3$$

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$$6.40 = 250K_3$$

And three K_3 values may be computed (one for each equation) which are 7.60×10^{-2}, 4.89×10^{-2}, and 2.56×10^{-2}. Since these K_3 values are all different, a linear rate law is not a possibility, and, by process of elimination, a logarithmic expression is obeyed.

(b) In order to determine the value of W after 3500 min, it is first necessary that we solve for the K_4, K_5, and K_6 constants of Equation 17.36. One way this may be accomplished is to use an equation solver. In some instances it is desirable to express Equation 17.36 in exponential form, as

$$K_5 + K_6 = 10^{W/K_4}$$

For some solvers, using the above expression, the following instructions can be used:

```
K5 *t1 + K6 = 10^(W1/K4)
K5 *t2 + K6 = 10^(W2/K4)
K5 *t3 + K6 = 10^(W3/K4)

t1 = 25;        W1 = 1.90
t2 = 75;        W2 = 3.67
t3 = 250;       W3 = 6.40
```

The resulting solutions—i.e., values for the K parameters—are

$K_4 = 6.50$
$K_5 = 0.0342$
$K_6 = 1.1055$

Now solving Equation 17.36 for W at a time of 3500 min

$$W = K_4 \log \left(K_5 t + K_6\right)$$

$$= 6.50 \log \left[(0.0342)(3500 \text{ min}) + 1.1055\right]$$

$$= 13.53 \text{ mg/cm}^2$$

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DESIGN PROBLEMS

17.D1 *A brine solution is used as a cooling medium in a steel heat exchanger. The brine is circulated within the heat exchanger and contains some dissolved oxygen. Suggest three methods, other than cathodic protection, for reducing corrosion of the steel by the brine. Explain the rationale for each suggestion.*

Solution

Possible methods that may be used to reduce corrosion of the heat exchanger by the brine solution are as follows:

(1) Reduce the temperature of the brine; normally, the rate of a corrosion reaction increases with increasing temperature.

(2) Change the composition of the brine; the corrosion rate is often quite dependent on the composition of the corrosion environment.

(3) Remove as much dissolved oxygen as possible. Under some circumstances, the dissolved oxygen may form bubbles, which can lead to erosion-corrosion damage.

(4) Minimize the number of bends and/or changes in pipe contours in order to minimize erosion-corrosion.

(5) Add inhibitors.

(6) Avoid connections between different metal alloys.

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17.D2 *Suggest an appropriate material for each of the following applications, and, if necessary, recommend corrosion prevention measures that should be taken. Justify your suggestions.*

(a) Laboratory bottles to contain relatively dilute solutions of nitric acid

(b) Barrels to contain benzene

(c) Pipe to transport hot alkaline (basic) solutions

(d) Underground tanks to store large quantities of high-purity water

(e) Architectural trim for high-rise buildings

Solution

This question asks that we suggest appropriate materials, and if necessary, recommend corrosion prevention measures that should be taken for several specific applications. These are as follows:

(a) Laboratory bottles to contain relatively dilute solutions of nitric acid. Probably the best material for this application would be polytetrafluoroethylene (PTFE). The reasons for this are: (1) it is flexible and will not easily break if dropped; and (2) PTFE is resistant to this type of acid, as noted in Table 17.4.

(b) Barrels to contain benzene. Poly(ethylene terephthalate) (PET) would be suited for this application, since it is resistant to degradation by benzene (Table 17.4), and is less expensive than the other two materials listed in Table 17.4 (see Appendix C).

(c) Pipe to transport hot alkaline (basic) solutions. The best material for this application would probably be a nickel alloy (Section 13.3). Polymeric materials listed in Table 17.4 would not be suitable inasmuch as the solutions are hot.

(d) Underground tanks to store large quantities of high-purity water. The outside of the tanks should probably be some type of low-carbon steel that is cathodically protected (Sections 17.8 and 17.9). Inside the steel shell should be coated with an inert polymeric material; polytetrafluoroethylene or some other fluorocarbon would probably be the material of choice (Table 17.4).

(e) Architectural trim for high-rise buildings. The most likely candidate for this application would probably be an aluminum alloy. Aluminum and its alloys are relatively corrosion resistant in normal atmospheres (Section 16.8), retain their lustrous appearance, and are relatively inexpensive (Appendix C).

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17.D3 *Each student (or group of students) is to find a real-life corrosion problem that has not been solved, conduct a thorough investigation as to the cause(s) and type(s) of corrosion, and, finally, propose possible solutions for the problem, indicating which of the solutions is best and why. Submit a report that addresses the above issues.*

Each student or group of students is to submit their own report on a corrosion problem investigation that was conducted.

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CHAPTER 18

ELECTRICAL PROPERTIES

PROBLEM SOLUTIONS

Ohm's Law

Electrical Conductivity

18.1 *(a) Compute the electrical conductivity of a 5.1-mm (0.2-in.) diameter cylindrical silicon specimen 51 mm (2 in.) long in which a current of 0.1 A passes in an axial direction. A voltage of 12.5 V is measured across two probes that are separated by 38 mm (1.5 in.).*

(b) Compute the resistance over the entire 51 mm (2 in.) of the specimen.

Solution

This problem calls for us to compute the electrical conductivity and resistance of a silicon specimen.

(a) We use Equations 18.3 and 18.4 for the conductivity, as

$$\sigma = \frac{1}{\rho} = \frac{Il}{VA} = \frac{Il}{V\pi\left(\frac{d}{2}\right)^2}$$

And, incorporating values for the several parameters provided in the problem statement, leads to

$$\sigma = \frac{(0.1\text{ A})\left(38 \times 10^{-3}\text{ m}\right)}{(12.5\text{ V})(\pi)\left(\frac{5.1 \times 10^{-3}\text{ m}}{2}\right)^2} = 14.9\ (\Omega\text{ - m})^{-1}$$

(b) The resistance, R, may be computed using Equations 18.2 and 18.4, as

$$R = \frac{\rho l}{A} = \frac{l}{\sigma A} = \frac{l}{\sigma\pi\left(\frac{d}{2}\right)^2}$$

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$$= \frac{51 \times 10^{-3}\ \text{m}}{\left[14.9\ \ (\Omega - \text{m})^{-1}\right](\pi)\left(\frac{5.1 \times 10^{-3}\ \text{m}}{2}\right)^2} = 168\ \ \Omega$$

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18.2 *A copper wire 100 m long must experience a voltage drop of less than 1.5 V when a current of 2.5 A passes through it. Using the data in Table 18.1, compute the minimum diameter of the wire.*

Solution

For this problem, given that a copper wire 100 m long must experience a voltage drop of less than 1.5 V when a current of 2.5 A passes through it, we are to compute the minimum diameter of the wire. Combining Equations 18.3 and 18.4 and solving for the cross-sectional area A leads to

$$A = \frac{Il\rho}{V} = \frac{Il}{V\sigma}$$

From Table 18.1, for copper $\sigma = 6.0 \times 10^7\ (\Omega\text{-m})^{-1}$. Furthermore, inasmuch as $A = \pi\left(\frac{d}{2}\right)^2$ for a cylindrical wire, then

$$\pi\left(\frac{d}{2}\right)^2 = \frac{Il}{V\sigma}$$

or

$$d = \sqrt{\frac{4Il}{\pi V\sigma}}$$

When values for the several parameters given in the problem statement are incorporated into this expression, we get

$$d = \sqrt{\frac{(4)(2.5\text{ A})(100\text{ m})}{(\pi)(1.5\text{ V})\left[6.0 \times 10^7\ (\Omega - \text{m})^{-1}\right]}}$$

$$= 1.88 \times 10^{-3}\text{ m} = 1.88\text{ mm}$$

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18.3 *An aluminum wire 4 mm in diameter is to offer a resistance of no more than 2.5 Ω. Using the data in Table 18.1, compute the maximum wire length.*

Solution

This problem asks that we compute, for an aluminum wire 4 mm in diameter, the maximum length such that the resistance will not exceed 2.5 Ω. From Table 18.1 for aluminum, $\sigma = 3.8 \times 10^7\ (\Omega\text{-m})^{-1}$. If d is the diameter then, combining Equations 18.2 and 18.4 leads to

$$l = \frac{RA}{\rho} = R\sigma A = R\sigma\pi\left(\frac{d}{2}\right)^2$$

$$= (2.5\ \Omega)\left[3.8 \times 10^7\ (\Omega - \text{m})^{-1}\right](\pi)\left(\frac{4 \times 10^{-3}\ \text{m}}{2}\right)^2 = 1194\ \text{m}$$

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18.4 *Demonstrate that the two Ohm's law expressions, Equations 18.1 and 18.5, are equivalent.*

Solution

Let us demonstrate, by appropriate substitution and algebraic manipulation, that Equation 18.5 may be made to take the form of Equation 18.1. Now, Equation 18.5 is just

$$J = \sigma E$$

(In this equation we represent the electric field with an "*E*".) But, by definition, *J* is just the current density, the current per unit cross-sectional area, or $J = \frac{I}{A}$. Also, the electric field is defined by $E = \frac{V}{l}$. And, substituting these expressions into Equation 18.5 leads to

$$\frac{I}{A} = \sigma \frac{V}{l}$$

But, from Equations 18.2 and 18.4

$$\sigma = \frac{l}{RA}$$

and

$$\frac{I}{A} = \left(\frac{l}{RA}\right)\left(\frac{V}{l}\right)$$

Solving for *V* from this expression gives *V* = *IR*, which is just Equation 18.1.

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18.5 *(a) Using the data in Table 18.1, compute the resistance of a copper wire 3 mm (0.12 in.) in diameter and 2 m (78.7 in.) long. (b) What would be the current flow if the potential drop across the ends of the wire is 0.05 V? (c) What is the current density? (d) What is the magnitude of the electric field across the ends of the wire?*

Solution

(a) In order to compute the resistance of this copper wire it is necessary to employ Equations 18.2 and 18.4. Solving for the resistance in terms of the conductivity,

$$R = \frac{\rho l}{A} = \frac{l}{\sigma A} = \frac{l}{\sigma\pi\left(\frac{d}{2}\right)^2}$$

From Table 18.1, the conductivity of copper is $6.0 \times 10^7\ (\Omega\text{-m})^{-1}$, and

$$R = \frac{l}{\sigma\pi\left(\frac{d}{2}\right)^2} = \frac{2\ \text{m}}{\left[6.0\ \times 10^7\ (\Omega - \text{m})^{-1}\right](\pi)\left(\frac{3\ \times 10^{-3}\ \text{m}}{2}\right)^2}$$

$$= 4.7 \times 10^{-3}\ \Omega$$

(b) If $V = 0.05$ V then, from Equation 18.1

$$I = \frac{V}{R} = \frac{0.05\ \text{V}}{4.7\ \times 10^{-3}\ \Omega} = 10.6\ \ \text{A}$$

(c) The current density is just

$$J = \frac{I}{A} = \frac{I}{\pi\left(\frac{d}{2}\right)^2} = \frac{10.6\ \ \text{A}}{\pi\left(\frac{3\ \times 10^{-3}\ \text{m}}{2}\right)^2} = 1.5 \times 10^6\ \ \text{A/m}^2$$

(d) The electric field is just

$$E = \frac{V}{l} = \frac{0.05\ \text{V}}{2\ \text{m}} = 2.5\ \times\ 10^{-2}\ \ \text{V/m}$$

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Electronic and Ionic Conduction

18.6 *What is the distinction between electronic and ionic conduction?*

Solution

When a current arises from a flow of electrons, the conduction is termed *electronic*; for *ionic conduction*, the current results from the net motion of charged ions.

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Energy Band Structures in Solids

18.7 *How does the electron structure of an isolated atom differ from that of a solid material?*

Solution

For an isolated atom, there exist discrete electron energy states (arranged into shells and subshells); each state may be occupied by, at most, two electrons, which must have opposite spins. On the other hand, an electron band structure is found for solid materials; within each band exist closely spaced yet discrete electron states, each of which may be occupied by, at most, two electrons, having opposite spins. The number of electron states in each band will equal the total number of corresponding states contributed by all of the atoms in the solid.

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Conduction in Terms of Band and Atomic Bonding Models

18.8 *In terms of electron energy band structure, discuss reasons for the difference in electrical conductivity between metals, semiconductors, and insulators.*

Solution

For metallic materials, there are vacant electron energy states adjacent to the highest filled state; thus, very little energy is required to excite large numbers of electrons into conducting states. These electrons are those that participate in the conduction process, and, because there are so many of them, metals are good electrical conductors.

There are no empty electron states adjacent to and above filled states for semiconductors and insulators, but rather, an energy band gap across which electrons must be excited in order to participate in the conduction process. Thermal excitation of electrons will occur, and the number of electrons excited will be less than for metals, and will depend on the band gap energy. For semiconductors, the band gap is narrower than for insulators; consequently, at a specific temperature more electrons will be excited for semiconductors, giving rise to higher conductivities.

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Electron Mobility

18.9 *Briefly tell what is meant by the drift velocity and mobility of a free electron.*

Solution

The drift velocity of a free electron is the average electron velocity in the direction of the force imposed by an electric field.

The mobility is the proportionality constant between the drift velocity and the electric field. It is also a measure of the frequency of scattering events (and is inversely proportional to the frequency of scattering).

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18.10 *(a) Calculate the drift velocity of electrons in germanium at room temperature and when the magnitude of the electric field is 1000 V/m. (b) Under these circumstances, how long does it take an electron to traverse a 25-mm (1-in.) length of crystal?*

Solution

(a) The drift velocity of electrons in Ge may be determined using Equation 18.7. Since the room temperature mobility of electrons is 0.38 m^2/V-s (Table 18.3), and the electric field is 1000 V/m (as stipulated in the problem statement),

$$v_d = \mu_e E$$

$$= (0.38\ m^2/V\text{-}s)(1000\ V/m) = 380\ m/s$$

(b) The time, t, required to traverse a given length, l (= 25 mm), is just

$$t = \frac{l}{v_d} = \frac{25 \times 10^{-3}\ m}{380\ m/s} = 6.6 \times 10^{-5}\ s$$

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18.11 *At room temperature the electrical conductivity and the electron mobility for copper are 6.0×10^7 $(\Omega\text{-m})^{-1}$ and 0.0030 m^2/V-s, respectively. (a) Compute the number of free electrons per cubic meter for copper at room temperature. (b) What is the number of free electrons per copper atom? Assume a density of 8.9 g/cm^3.*

Solution

(a) The number of free electrons per cubic meter for copper at room temperature may be computed using Equation 18.8 as

$$n = \frac{\sigma}{|e|\,\mu_e}$$

$$= \frac{6.0 \times 10^7\ (\Omega - \text{m})^{-1}}{(1.602 \times 10^{-19}\ \text{C})(0.003\ \text{m}^2/\text{V-s})}$$

$$= 1.25 \times 10^{29}\ \text{m}^{-3}$$

(b) In order to calculate the number of free electrons per copper atom, we must first determine the number of copper atoms per cubic meter, N_{Cu}. From Equation 4.2 (and using the atomic weight value for Cu found inside the front cover—viz. 63.55 g/mol)

$$N_{Cu} = \frac{N_A \rho'}{A_{Cu}}$$

$$= \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(8.9\ \text{g/cm}^3)(10^6\ \text{cm}^3/\text{m}^3)}{63.55\ \text{g/mol}}$$

$$= 8.43 \times 10^{28}\ \text{m}^{-3}$$

(*Note*: in the above expression, density is represented by ρ' in order to avoid confusion with resistivity which is designated by ρ.) And, finally, the number of free electrons per aluminum atom is just n/N_{Cu}

$$\frac{n}{N_{Cul}} = \frac{1.25 \times 10^{29}\ \text{m}^{-3}}{8.43 \times 10^{28}\ \text{m}^{-3}} = 1.48$$

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18.12 *(a) Calculate the number of free electrons per cubic meter for gold assuming that there are 1.5 free electrons per gold atom. The electrical conductivity and density for Au are 4.3 × 10^7 (Ω-m)$^{-1}$ and 19.32 g/cm^3, respectively. (b) Now compute the electron mobility for Au.*

Solution

(a) This portion of the problem asks that we calculate, for gold, the number of free electrons per cubic meter (n) given that there are 1.5 free electrons per gold atom, that the electrical conductivity is 4.3×10^7 $(\Omega\text{-m})^{-1}$, and that the density (ρ'_{Au}) is 19.32 g/cm^3. (Note: in this discussion, the density of silver is represented by ρ'_{Au} in order to avoid confusion with resistivity which is designated by ρ.) Since $n = 1.5N_{Au}$, and N_{Au} is defined in Equation 4.2 (and using the atomic weight of Au found inside the front cover—viz 196.97 g/mol), then

$$n = 1.5N_{Au} = 1.5\left[\frac{\rho'_{Au}N_A}{A_{Au}}\right]$$

$$= 1.5\left[\frac{(19.32\ \text{g/cm}^3)(6.022 \times 10^{23}\ \text{atoms/mol})}{196.97\ \text{g/mol}}\right]$$

$$= 8.86 \times 10^{22}\ \text{cm}^{-3} = 8.86 \times 10^{28}\ \text{m}^{-3}$$

(b) Now we are asked to compute the electron mobility, μ_e. Using Equation 18.8

$$\mu_e = \frac{\sigma}{n|e|}$$

$$= \frac{4.3 \times 10^7\ (\Omega - \text{m})^{-1}}{(8.86 \times 10^{28}\ \text{m}^{-3})(1.602 \times 10^{-19}\ \text{C})} = 3.03 \times 10^{-3}\ \text{m}^2/\text{V-s}$$

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Electrical Resistivity of Metals

18.13 *From Figure 18.38, estimate the value of A in Equation 18.11 for zinc as an impurity in copper–zinc alloys.*

Solution

We want to solve for the parameter A in Equation 18.11 using the data in Figure 18.38. From Equation 18.11

$$A = \frac{\rho_i}{c_i (1 - c_i)}$$

However, the data plotted in Figure 18.38 is the total resistivity, ρ_{total}, and includes both impurity (ρ_i) and thermal (ρ_t) contributions (Equation 18.9). The value of ρ_t is taken as the resistivity at $c_i = 0$ in Figure 18.38, which has a value of 1.7×10^{-8} (Ω-m); this must be subtracted out. Below are tabulated values of A determined at $c_i = 0.10$, 0.20, and 0.30, including other data that were used in the computations. (*Note:* the c_i values were taken from the upper horizontal axis of Figure 18.38, since it is graduated in atom percent zinc.)

c_i	$1 - c_i$	ρ_{total} (Ω-m)	ρ_i (Ω-m)	A (Ω-m)
0.10	0.90	4.0×10^{-8}	2.3×10^{-8}	2.56×10^{-7}
0.20	0.80	5.4×10^{-8}	3.7×10^{-8}	2.31×10^{-7}
0.30	0.70	6.15×10^{-8}	4.45×10^{-8}	2.12×10^{-7}

So, there is a slight decrease of A with increasing c_i.

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18.14 *(a) Using the data in Figure 18.8, determine the values of ρ_0 and a from Equation 18.10 for pure copper. Take the temperature T to be in degrees Celsius. (b) Determine the value of A in Equation 18.11 for nickel as an impurity in copper, using the data in Figure 18.8. (c) Using the results of parts (a) and (b), estimate the electrical resistivity of copper containing 1.75 at% Ni at 100°C.*

Solution

(a) Perhaps the easiest way to determine the values of ρ_0 and a in Equation 18.10 for pure copper in Figure 18.8, is to set up two simultaneous equations using two resistivity values (labeled ρ_{t1} and ρ_{t2}) taken at two corresponding temperatures (T_1 and T_2). Thus,

$$\rho_{t1} = \rho_0 + aT_1$$

$$\rho_{t2} = \rho_0 + aT_2$$

And solving these equations simultaneously lead to the following expressions for a and ρ_0:

$$a = \frac{\rho_{t1} - \rho_{t2}}{T_1 - T_2}$$

$$\rho_0 = \rho_{t1} - T_1\left[\frac{\rho_{t1} - \rho_{t2}}{T_1 - T_2}\right]$$

$$= \rho_{t2} - T_2\left[\frac{\rho_{t1} - \rho_{t2}}{T_1 - T_2}\right]$$

From Figure 18.8, let us take $T_1 = -150°C$, $T_2 = -50°C$, which gives $\rho_{t1} = 0.6 \times 10^{-8}$ (Ω-m), and $\rho_{t2} = 1.25 \times 10^{-8}$ (Ω-m). Therefore

$$a = \frac{\rho_{t1} - \rho_{t2}}{T_1 - T_2}$$

$$= \frac{\left[\left(0.6 \times 10^{-8}\right) - \left(1.25 \times 10^{-8}\right)\right](\Omega\text{-m})}{-150°C - (-50°C)}$$

$$6.5 \times 10^{-11}\ (\Omega\text{-m})/°C$$

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and

$$\rho_0 = \rho_{t1} - T_1\left[\frac{\rho_{t1} - \rho_{t2}}{T_1 - T_2}\right]$$

$$= \left(0.6 \times 10^{-8}\right) - (-150)\,\frac{\left[\left(0.6 \times 10^{-8}\right) - \left(1.25 \times 10^{-8}\right)\right](\Omega\text{-m})}{-150°\text{C} - (-50°\text{C})}$$

$$= 1.58 \times 10^{-8}\ (\Omega\text{-m})$$

(b) For this part of the problem, we want to calculate A from Equation 18.11

$$\rho_i = Ac_i(1 - c_i)$$

In Figure 18.8, curves are plotted for three c_i values (0.0112, 0.0216, and 0.0332). Let us find A for each of these c_i's by taking a ρ_{total} from each curve at some temperature (say 0°C) and then subtracting out ρ_i for pure copper at this same temperature (which is 1.7×10^{-8} Ω-m). Below is tabulated values of A determined from these three c_i values, and other data that were used in the computations.

c_i	$1 - c_i$	ρ_{total} (Ω-m)	ρ_i (Ω-m)	A (Ω-m)
0.0112	0.989	3.0×10^{-8}	1.3×10^{-8}	1.17×10^{-6}
0.0216	0.978	4.2×10^{-8}	2.5×10^{-8}	1.18×10^{-6}
0.0332	0.967	5.5×10^{-8}	3.8×10^{-8}	1.18×10^{-6}

The average of these three A values is 1.18×10^{-6} (Ω-m).

(c) We use the results of parts (a) and (b) to estimate the electrical resistivity of copper containing 1.75 at% Ni ($c_i = 0.0175$) at 100°C. The total resistivity is just

$$\rho_{\text{total}} = \rho_t + \rho_i$$

Or incorporating the expressions for ρ_t and ρ_i from Equations 18.10 and 18.11, and the values of ρ_0, a, and A determined above, leads to

$$\rho_{\text{total}} = (\rho_0 + aT) + Ac_i(1 - c_i)$$

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$$= \left\{1.58 \times 10^{-8}\ (\Omega\text{-m}) + \left[6.5 \times 10^{-11}\ (\Omega\text{-m})/°\text{C}\right](100°\text{C})\right\}$$
$$+ \left\{\left[1.18 \times 10^{-6}\ (\Omega\text{-m})\right](0.0175)(1 - 0.0175)\right\}$$

$$= 4.25 \times 10^{-8}\ (\Omega\text{-m})$$

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18.15 *Determine the electrical conductivity of a Cu-Ni alloy that has a yield strength of 125 MPa (18,000 psi). You will find Figure 7.16 helpful.*

Solution

We are asked to determine the electrical conductivity of a Cu-Ni alloy that has a yield strength of 125 MPa. From Figure 7.16*b*, the composition of an alloy having this tensile strength is about 20 wt% Ni. For this composition, the resistivity is about 27×10^{-8} Ω-m (Figure 18.9). And since the conductivity is the reciprocal of the resistivity, Equation 18.4, we have

$$\sigma = \frac{1}{\rho} = \frac{1}{27 \times 10^{-8}\ \Omega - \mathrm{m}} = 3.70 \times 10^{6}\ (\Omega - \mathrm{m})^{-1}$$

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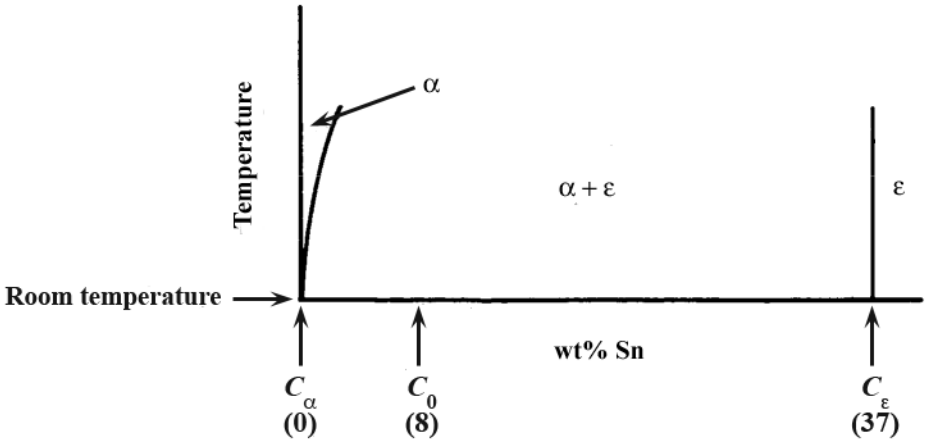
18.16 *Tin bronze has a composition of 92 wt% Cu and 8 wt% Sn, and consists of two phases at room temperature: an α phase, which is copper containing a very small amount of tin in solid solution, and an ε phase, which consists of approximately 37 wt% Sn. Compute the room temperature conductivity of this alloy given the following data:*

Phase	***Electrical Resistivity (Ω-m)***	***Density (g/cm^3)***
α	1.88×10^{-8}	8.94
ε	5.32×10^{-7}	8.25

Solution

This problem asks for us to compute the room-temperature conductivity of a two-phase Cu-Sn alloy which composition is 92 wt% Cu-8 wt% Sn. It is first necessary for us to determine the volume fractions of the α and ε phases, after which the resistivity (and subsequently, the conductivity) may be calculated using Equation 18.12. Weight fractions of the two phases are first calculated using the phase diagram information provided in the problem.

We may represent a portion of the phase diagram near room temperature as follows:



Applying the lever rule to this situation

$$W_\alpha = \frac{C_\varepsilon - C_0}{C_\varepsilon - C_\alpha} = \frac{37 - 8}{37 - 0} = 0.784$$

$$W_\varepsilon = \frac{C_0 - C_\alpha}{C_\varepsilon - C_\alpha} = \frac{8 - 0}{37 - 0} = 0.216$$

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We must now convert these mass fractions into volume fractions using the phase densities given in the problem statement. (*Note:* in the following expressions, density is represented by ρ' in order to avoid confusion with resistivity which is designated by ρ.) Utilization of Equations 9.6a and 9.6b leads to

$$V_\alpha = \frac{\dfrac{W_\alpha}{\rho'_\alpha}}{\dfrac{W_\alpha}{\rho'_\alpha} + \dfrac{W_\varepsilon}{\rho'_\varepsilon}}$$

$$= \frac{\dfrac{0.784}{8.94\ \text{g/cm}^3}}{\dfrac{0.784}{8.94\ \text{g/cm}^3} + \dfrac{0.216}{8.25\ \text{g/cm}^3}}$$

$$= 0.770$$

$$V_\varepsilon = \frac{\dfrac{W_\varepsilon}{\rho'_\varepsilon}}{\dfrac{W_\alpha}{\rho'_\alpha} + \dfrac{W_\varepsilon}{\rho'_\varepsilon}}$$

$$= \frac{\dfrac{0.216}{8.25\ \text{g/cm}^3}}{\dfrac{0.784}{8.94\ \text{g/cm}^3} + \dfrac{0.216}{8.25\ \text{g/cm}^3}}$$

$$= 0.230$$

Now, using Equation 18.12

$$\rho = \rho_\alpha V_\alpha + \rho_\varepsilon V_\varepsilon$$

$$= (1.88 \times 10^{-8}\ \Omega\text{-m})(0.770) + (5.32 \times 10^{-7}\ \Omega\text{-m})(0.230)$$

$$= 1.368 \times 10^{-7}\ \Omega\text{-m}$$

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Finally, for the conductivity (Equation 18.4)

$$\sigma = \frac{1}{\rho} = \frac{1}{1.368 \times 10^{-7}\ \Omega - \mathrm{m}} = 7.31\ \times\ 10^{6}\ (\Omega\text{ - m})^{-1}$$

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18.17 *A cylindrical metal wire 2 mm (0.08 in.) in diameter is required to carry a current of 10 A with a minimum of 0.03 V drop per foot (300 mm) of wire. Which of the metals and alloys listed in Table 18.1 are possible candidates?*

Solution

We are asked to select which of several metals may be used for a 2 mm diameter wire to carry 10 A, and have a voltage drop less than 0.03 V per foot (300 mm). Using Equations 18.3 and 18.4, let us determine the minimum conductivity required, and then select from Table 18.1, those metals that have conductivities greater than this value. Combining Equations 18.3 and 18.4, the minimum conductivity is just

$$\sigma = \frac{1}{\rho} = \frac{Il}{VA} = \frac{Il}{V\pi\left(\frac{d}{2}\right)^2}$$

$$= \frac{(10\text{ A})(300 \times 10^{-3}\text{ m})}{(0.03\text{ V})\ (\pi)\left(\frac{2 \times 10^{-3}\text{ m}}{2}\right)^2} = 3.2 \times 10^{7}\ (\Omega\text{-m})^{-1}$$

Thus, from Table 18.1, only aluminum, gold, copper, and silver are candidates.

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Intrinsic Semiconduction

18.18 *(a) Using the data presented in Figure 18.16, determine the number of free electrons per atom for intrinsic germanium and silicon at room temperature (298 K). The densities for Ge and Si are 5.32 and 2.33 g/cm^3, respectively.*

(b) Now explain the difference in these free-electron-per-atom values.

Solution

(a) For this part of the problem, we first read, from Figure 18.16, the number of free electrons (i.e., the intrinsic carrier concentration) at room temperature (298 K). These values are $n_i(\text{Ge}) = 5 \times 10^{19}$ m^{-3} and $n_i(\text{Si}) = 7 \times 10^{16}$ m^{-3}.

Now, the number of atoms per cubic meter for Ge and Si (N_{Ge} and N_{Si}, respectively) may be determined using Equation 4.2 which involves the densities (ρ'_{Ge} and ρ'_{Si}) and atomic weights (A_{Ge} and A_{Si}). (*Note:* here we use ρ' to represent density in order to avoid confusion with resistivity, which is designated by ρ. Also, the atomic weights for Ge and Si, 72.64 and 28.09 g/mol, respectively, are found inside the front cover.) Therefore,

$$N_{\text{Ge}} = \frac{N_{\text{A}}\rho'_{\text{Ge}}}{A_{\text{Ge}}}$$

$$= \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(5.32\ \text{g/cm}^3)(10^6\ \text{cm}^3/\text{m}^3)}{72.64\ \text{g/mol}}$$

$$= 4.41 \times 10^{28}\ \text{atoms/m}^3$$

Similarly, for Si

$$N_{\text{Si}} = \frac{N_{\text{A}}\rho'_{\text{Si}}}{A_{\text{Si}}}$$

$$= \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(2.33\ \text{g/cm}^3)(10^6\ \text{cm}^3/\text{m}^3)}{28.09\ \text{g/mol}}$$

$$= 5.00 \times 10^{28}\ \text{atoms/m}^3$$

Finally, the ratio of the number of free electrons per atom is calculated by dividing n_i by N. For Ge

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$$\frac{n_i(\text{Ge})}{N_{\text{Ge}}} = \frac{5 \times 10^{19} \text{ electrons/m}^3}{4.41 \times 10^{28} \text{ atoms/m}^3}$$

$$1.13 \times 10^{-9} \text{ electron/atom}$$

And, for Si

$$\frac{n_i(\text{Si})}{N_{\text{Si}}} = \frac{7 \times 10^{16} \text{ electrons/m}^3}{5.00 \times 10^{28} \text{ atoms/m}^3}$$

$$= 1.40 \times 10^{-12} \text{ electron/atom}$$

(b) The difference is due to the magnitudes of the band gap energies (Table 18.3). The band gap energy at room temperature for Si (1.11 eV) is larger than for Ge (0.67 eV), and, consequently, the probability of excitation across the band gap for a valence electron is much smaller for Si.

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18.19 *For intrinsic semiconductors, the intrinsic carrier concentration n_i depends on temperature as follows:*

$$n_i \propto \exp\left(-\frac{E_g}{2kT}\right) \tag{18.35a}$$

or taking natural logarithms,

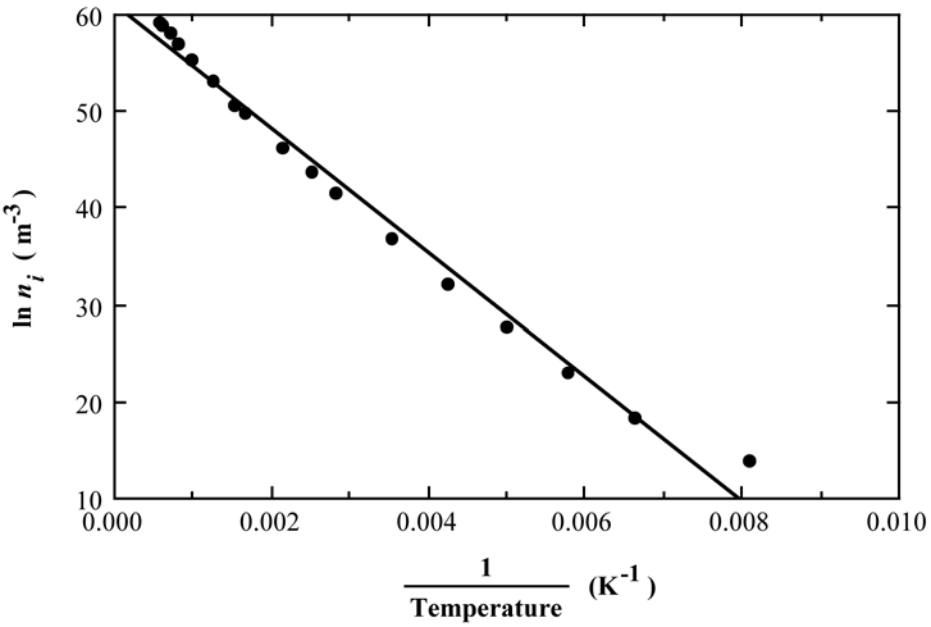
$$\ln n_i \propto -\frac{E_g}{2kT} \tag{18.35b}$$

Thus, a plot of ln n_i versus 1/T $(K)^{-1}$ should be linear and yield a slope of $-E_g/2k$. Using this information and the data presented in Figure 18.16, determine the band gap energies for silicon and germanium, and compare these values with those given in Table 18.3.

Solution

This problem asks that we make plots of ln n_i versus reciprocal temperature for both Si and Ge, using the data presented in Figure 18.16, and then determine the band gap energy for each material realizing that the slope of the resulting line is equal to $-E_g/2k$.

Below is shown such a plot for Si.



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The slope of the line is equal to

$$\text{Slope} = \frac{\Delta \ln \eta_i}{\Delta\left(\frac{1}{T}\right)} = \frac{\ln \eta_1 - \ln \eta_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

Let us take $1/T_1 = 0.001$ and $1/T_2 = 0.007$; their corresponding ln η values are ln $\eta_1 = 54.80$ and ln $\eta_2 = 16.00$. Incorporating these values into the above expression leads to a slope of

$$\text{Slope} = \frac{54.80 - 16.00}{0.001 - 0.007} = -6467$$

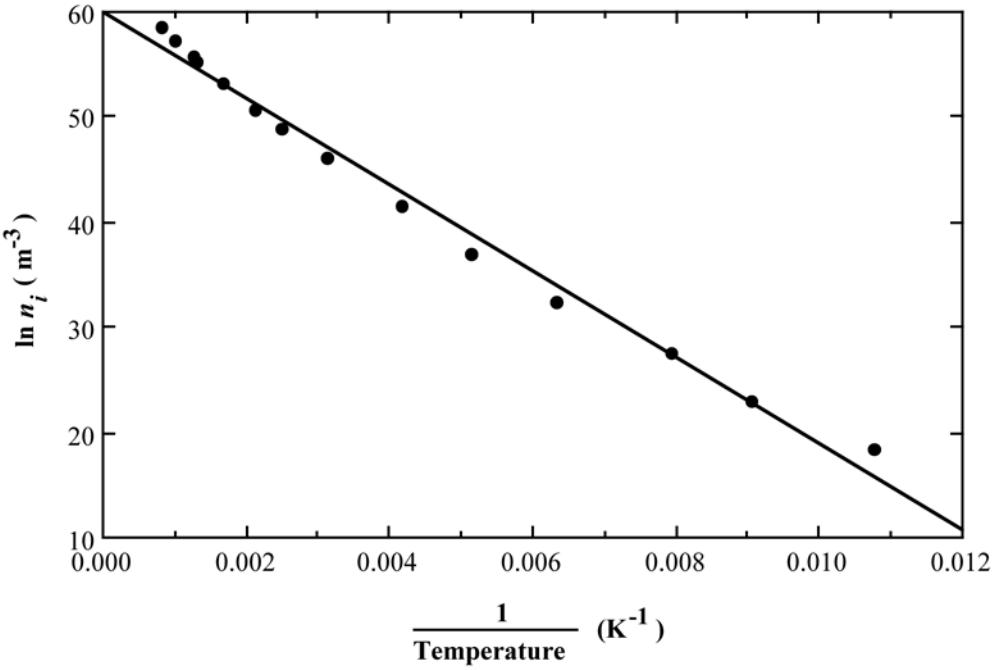
This slope leads to an E_g value of

$$E_g = -2k\,(\text{Slope})$$

$$= -2\left(8.62 \text{ x } 10^{-5} \text{ eV/K}\right)(-6467) = 1.115 \text{ eV}$$

The value cited in Table 18.3 is 1.11 eV.

Now for Ge, an analogous plot is shown below.



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We calculate the slope and band gap energy values in the manner outlined above. Let us take $1/T_1 = 0.001$ and $1/T_2 = 0.011$; their corresponding ln η values are ln $\eta_1 = 55.56$ and ln $\eta_2 = 14.80$. Incorporating these values into the above expression leads to a slope of

$$\text{Slope} = \frac{55.56 - 14.80}{0.001 - 0.011} = -4076$$

This slope leads to an E_g value of

$$E_g = -2k\,(\text{Slope})$$

$$= -2\left(8.62 \times 10^{-5}\ \text{eV/K}\right)(-4076) = 0.70\ \text{eV}$$

This value is in good agreement with the 0.67 eV cited in Table 18.3.

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18.20 *Briefly explain the presence of the factor 2 in the denominator of Equation 18.35a.*

Solution

The factor 2 in Equation 18.35a takes into account the creation of two charge carriers (an electron and a hole) for each valence-band-to-conduction-band intrinsic excitation; both charge carriers may participate in the conduction process.

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18.21 *At room temperature the electrical conductivity of PbTe is 500 $(\Omega\text{-m})^{-1}$, whereas the electron and hole mobilities are 0.16 and 0.075 m^2/V-s, respectively. Compute the intrinsic carrier concentration for PbTe at room temperature.*

Solution

In this problem we are asked to compute the intrinsic carrier concentration for PbTe at room temperature. Since the conductivity and both electron and hole mobilities are provided in the problem statement, all we need do is solve for n and p (i.e., n_i) using Equation 18.15. Thus,

$$n_i = \frac{\sigma}{|e|(\mu_e + \mu_h)}$$

$$= \frac{500\ (\Omega\text{-m})^{-1}}{(1.602 \times 10^{-19}\ \text{C})(0.16 + 0.075)\ \ \text{m}^2/\text{V-s}}$$

$$= 1.33 \times 10^{22}\ \text{m}^{-3}$$

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18.22 *Is it possible for compound semiconductors to exhibit intrinsic behavior? Explain your answer.*

Solution

Yes, compound semiconductors can exhibit intrinsic behavior. They will be intrinsic even though they are composed of two different elements as long as the electrical behavior is not influenced by the presence of other elements.

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18.23 *For each of the following pairs of semiconductors, decide which will have the smaller band gap energy, E_g, and then cite the reason for your choice. (a) ZnS and CdSe, (b) Si and C (diamond), (c) Al_2O_3 and ZnTe, (d) InSb and ZnSe, and (e) GaAs and AlP.*

Solution

This problem calls for us to decide for each of several pairs of semiconductors, which will have the smaller band gap energy and then cite a reason for the choice.

(a) Cadmium selenide will have a smaller band gap energy than zinc sulfide. Both are II-VI compounds, and Cd and Se are both lower vertically in the periodic table (Figure 2.6) than Zn and S. In moving from top to bottom down the periodic table, E_g decreases.

(b) Silicon will have a smaller band gap energy than diamond since Si is lower in column IVA of the periodic table than is C.

(c) Zinc telluride will have a smaller band gap energy that aluminum oxide. There is a greater disparity between the electronegativities for aluminum and oxygen [1.5 versus 3.5 (Figure 2.7)] than for zinc and tellurium (1.6 and 2.1). For binary compounds, the larger the difference between the electronegativities of the elements, the greater the band gap energy.

(d) Indium antimonide will have a smaller band gap energy than zinc selenide. These materials are III-V and II-VI compounds, respectively; Thus, in the periodic table, In and Sb are closer together horizontally than are Zn and Se. Furthermore, both In and Sb reside below Zn and Se in the periodic table.

(e) Gallium arsenide will have a smaller band gap energy than aluminum phosphide. Both are III-V compounds, and Ga and As are both lower vertically in the periodic table than Al and P.

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Extrinsic Semiconduction

18.24 *Define the following terms as they pertain to semiconducting materials: intrinsic, extrinsic, compound, elemental. Now provide an example of each.*

Solution

These semiconductor terms are defined in the Glossary. Examples are as follows: intrinsic--high purity (undoped) Si, GaAs, CdS, etc.; extrinsic--P-doped Ge, B-doped Si, S-doped GaP, etc.; compound--GaAs, InP, CdS, etc.; elemental--Ge and Si.

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18.25 *An n-type semiconductor is known to have an electron concentration of 3×10^{18} m^{-3}. If the electron drift velocity is 100 m/s in an electric field of 500 V/m, calculate the conductivity of this material.*

Solution

The conductivity of this material may be computed using Equation 18.16. But before this is possible, it is necessary to calculate the value of μ_e from Equation 18.7. Thus, the electron mobility is equal to

$$\mu_e = \frac{v_d}{E}$$

$$= \frac{100 \text{ m/s}}{500 \text{ V/m}} = 0.20 \text{ m}^2/\text{V}-\text{s}$$

Thus, from Equation 18.16, the conductivity is

$$\sigma = n|e|\mu_e$$

$$= \left(3 \times 10^{18} \text{ m}^{-3}\right)\left(1.602 \times 10^{-19} \text{ C}\right)\left(0.20 \text{ m}^2/\text{V}-\text{s}\right)$$

$$= 0.096 \ (\Omega\text{-m})^{-1}$$

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18.26 *(a) In your own words, explain how donor impurities in semiconductors give rise to free electrons in numbers in excess of those generated by valence band–conduction band excitations. (b) Also explain how acceptor impurities give rise to holes in numbers in excess of those generated by valence band–conduction band excitations.*

The explanations called for are found in Section 18.11.

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18.27 *(a) Explain why no hole is generated by the electron excitation involving a donor impurity atom. (b) Explain why no free electron is generated by the electron excitation involving an acceptor impurity atom.*

Solution

(a) No hole is generated by an electron excitation involving a donor impurity atom because the excitation comes from a level within the band gap, and thus, no missing electron is created within the normally filled valence band.

(b) No free electron is generated by an electron excitation involving an acceptor impurity atom because the electron is excited from the valence band into the impurity level within the band gap; no free electron is introduced into the conduction band.

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18.28 *Will each of the following elements act as a donor or an acceptor when added to the indicated semiconducting material? Assume that the impurity elements are substitutional.*

Impurity	***Semiconductor***
P	*Ge*
S	*AlP*
In	*CdTe*
Al	*Si*
Cd	*GaAs*
Sb	*ZnSe*

Solution

Phosphorus will act as a donor in Ge. Since it (P) is from group VA of the periodic table (Figure 2.6), a P atom has one more valence electron than a Ge atom.

Sulfur will act as a donor in AlP. Since S is from group VIA of the periodic table, it will substitute for P; also, an S atom has one more valence electron than a P atom.

Indium will act as a donor in CdTe. Since In is from group IIIA of the periodic table, it will substitute for Cd; furthermore, an In atom has one more valence electron than a Cd atom.

Aluminum will act as an acceptor in Si. Since it (Al) is from group IIIA of the periodic table (Figure 2.6), an Al atom has one less valence electron than a Si atom.

Cadmium will act as an acceptor in GaAs. Since Cd is from group IIB of the periodic table, it will substitute for Ga; furthermore, a Cd atom has one less valence electron than a Ga atom.

Antimony will act as an acceptor in ZnSe. Since Sb is from group VA of the periodic table, it will substitute for Se; and, an Sb atom has one less valence electron than an Se atom.

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18.29 *(a) The room-temperature electrical conductivity of a silicon specimen is 5.93×10^{-3} $(\Omega\text{-m})^{-1}$. The hole concentration is known to be 7.0×10^{17} m^{-3}. Using the electron and hole mobilities for silicon in Table 18.3, compute the electron concentration. (b) On the basis of the result in part (a), is the specimen intrinsic, n-type extrinsic, or p-type extrinsic? Why?*

Solution

(a) In this problem, for a Si specimen, we are given values for p $\left(7.0 \times 10^{17}\ \text{m}^{-3}\right)$ and σ $\left[5.93 \times 10^{-3}\ (\Omega\text{-m})^{-1}\right]$, while values for μ_h and μ_e (0.05 and 0.14 m^2/V-s, respectively) are found in Table 18.3. In order to solve for n we must use Equation 18.13, which, after rearrangement, leads to

$$n = \frac{\sigma - p|e|\mu_h}{|e|\mu_e}$$

$$= \frac{5.93 \times 10^{-3}\ (\Omega - \text{m})^{-1} - \left(7.0 \times 10^{17}\ \text{m}^{-3}\right)\left(1.602 \times 10^{-19}\ \text{C}\right)\left(0.05\ \text{m}^2/\text{V-s}\right)}{\left(1.602 \times 10^{-19}\ \text{C}\right)\left(0.14\ \text{m}^2/\text{V-s}\right)}$$

$$= 1.44 \times 10^{16}\ \text{m}^{-3}$$

(b) This material is p-type extrinsic since p $\left(7.0 \times 10^{17}\ \text{m}^{-3}\right)$ is greater than n $\left(1.44 \times 10^{16}\ \text{m}^{-3}\right)$.

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18.30 *Germanium to which 5×10^{22} m^{-3} Sb atoms have been added is an extrinsic semiconductor at room temperature, and virtually all the Sb atoms may be thought of as being ionized (i.e., one charge carrier exists for each Sb atom). (a) Is this material n-type or p-type? (b) Calculate the electrical conductivity of this material, assuming electron and hole mobilities of 0.1 and 0.05 m^2/V-s, respectively.*

Solution

(a) (a) This germanium material to which has been added 5×10^{22} m^{-3} Sb atoms is *n*-type since Sb is a donor in Ge. (Antimony is from group VA of the periodic table--Ge is from group IVA.)

(b) Since this material is *n*-type extrinsic, Equation 18.16 is valid. Furthermore, each Sb will donate a single electron, or the electron concentration is equal to the Sb concentration since all of the Sb atoms are ionized at room temperature; that is $n = 5 \times 10^{22}$ m^{-3}, and, as given in the problem statement, $\mu_e = 0.1$ m^2/V-s. Thus

$$\sigma = n|e|\mu_e$$

$$= \left(5 \times 10^{22}\ \text{m}^{-3}\right)\left(1.602 \times 10^{-19}\ \text{C}\right)\left(0.1\ \text{m}^2/\text{V-s}\right)$$

$$= 800\ (\Omega\text{-m})^{-1}$$

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18.31 *The following electrical characteristics have been determined for both intrinsic and p-type extrinsic indium phosphide (InP) at room temperature:*

	$\sigma\ (\Omega\text{-}m)^{-1}$	$n\ (m^{-3})$	$p\ (m^{-3})$
Intrinsic	2.5×10^{-6}	3.0×10^{13}	3.0×10^{13}
Extrinsic (n-type)	3.6×10^{-5}	4.5×10^{14}	2.0×10^{12}

Calculate electron and hole mobilities.

Solution

In order to solve for the electron and hole mobilities for InP, we must write conductivity expressions for the two materials, of the form of Equation 18.13—i.e.,

$$\sigma = n|e|\mu_e + p|e|\mu_h$$

For the intrinsic material

$$2.5 \times 10^{-6}\ (\Omega\text{-m})^{-1} = (3.0 \times 10^{13}\ \text{m}^{-3})(1.602 \times 10^{-19}\ \text{C})\,\mu_e + (3.0 \times 10^{13}\ \text{m}^{-3})(1.602 \times 10^{-19}\ \text{C})\,\mu_h$$

which reduces to

$$0.52 = \mu_e + \mu_h$$

Whereas, for the extrinsic InP

$$3.6 \times 10^{-5}\ (\Omega\text{-m})^{-1} = (4.5 \times 10^{14}\ \text{m}^{-3})(1.602 \times 10^{-19}\ \text{C})\,\mu_e + (2.0 \times 10^{12}\ \text{m}^{-3})(1.602 \times 10^{-19}\ \text{C})\,\mu_h$$

which may be simplified to

$$112.4 = 225\mu_e + \mu_h$$

Thus, we have two independent expressions with two unknown mobilities. Upon solving these equations simultaneously, we get $\mu_e = 0.50\ \text{m}^2/\text{V-s}$ and $\mu_h = 0.02\ \text{m}^2/\text{V-s}$.

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The Temperature Dependence of Carrier Concentration

18.32 *Calculate the conductivity of intrinsic silicon at 100°C.*

Solution

In order to estimate the electrical conductivity of intrinsic silicon at 100°C, we must employ Equation 18.15. However, before this is possible, it is necessary to determine values for n_i, μ_e, and μ_h. According to Figure 18.16, at 100°C (373 K), $n_i = 2 \times 10^{18}$ m^{-3}, whereas from the "$<10^{20}$ m^{-3}" curves of Figures 18.19a and 18.19b, at 100ºC (373 K), $\mu_e = 0.09$ m^2/V-s and $\mu_h = 0.032$ m^2/V-s (realizing that the mobility axes of these two plot are scaled logarithmically). Thus, the conductivity at 100°C is

$$\sigma = n_i |e| (\mu_e + \mu_h)$$

$$\sigma = (2 \times 10^{18}\ m^{-3})(1.602 \times 10^{-19}\ C)(0.09\ m^2/V\text{-}s + 0.032\ m^2/V\text{-}s)$$

$$= 0.039\ (\Omega\text{-}m)^{-1}$$

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18.33 *At temperatures near room temperature, the temperature dependence of the conductivity for intrinsic germanium is found to equal*

$$\sigma = CT^{-3/2} \exp\left(-\frac{E_g}{2kT}\right) \qquad (18.36)$$

where C is a temperature-independent constant and T is in Kelvins. Using Equation 18.36, calculate the intrinsic electrical conductivity of germanium at 150°C.

Solution

It first becomes necessary to solve for C in Equation 18.36 using the room-temperature (298 K) conductivity [2.2 $(\Omega\text{-m})^{-1}$] (Table 18.3). This is accomplished by taking natural logarithms of both sides of Equation 18.36 as

$$\ln \sigma = \ln C - \frac{3}{2}\ln T - \frac{E_g}{2kT}$$

and after rearranging and substitution of values for E_g (0.67 eV, Table 18.3), and the room-temperature conductivity, we get

$$\ln C = \ln \sigma + \frac{3}{2}\ln T + \frac{E_g}{2kT}$$

$$= \ln (2.2) + \frac{3}{2}\ln (298) + \frac{0.67 \text{ eV}}{(2)(8.62 \times 10^{-5} \text{ eV/K})(298 \text{ K})}$$

$$= 22.38$$

Now, again using Equation 18.36, we are able to compute the conductivity at 423 K (150°C)

$$\ln \sigma = \ln C - \frac{3}{2}\ln T - \frac{E_g}{2kT}$$

$$= 22.38 - \frac{3}{2}\ln (423 \text{ K}) - \frac{0.67 \text{ eV}}{(2)(8.62 \times 10^{-5} \text{ eV/K})(423 \text{ K})}$$

$$= 4.12$$

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which leads to

$$\sigma = e^{4.12} = 61.6\ (\Omega\text{-m})^{-1}.$$

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18.34 *Using Equation 18.36 and the results of Problem 18.33, determine the temperature at which the electrical conductivity of intrinsic germanium is 22.8 (Ω-m)$^{-1}$.*

Solution

This problem asks that we determine the temperature at which the electrical conductivity of intrinsic Ge is 22.8 (Ω-m)$^{-1}$, using Equation 18.36 and the results of Problem 18.33. First of all, taking logarithms of Equation 18.36

$$\ln \sigma = \ln C - \frac{3}{2}\ln T - \frac{E_g}{2kT}$$

And, from Problem 18.33 the value of ln C was determined to be 22.38. Using this and $\sigma = 22.8\ (\Omega\text{-m})^{-1}$, the above equation takes the form

$$\ln 22.8 = 22.38 - \frac{3}{2}\ln T - \frac{0.67\ \text{eV}}{(2)(8.62 \times 10^{-5}\ \text{eV/K})(T)}$$

In order to solve for T from the above expression it is necessary to use an equation solver. For some solvers, the following set of instructions may be used:

ln(22.8) = 22.38 –1.5*ln(T) – 0.67/(2*8.62*10^-5*T)

The resulting solution is $T = 375$, which value is the temperature in K; this corresponds to T(ºC) = 375 – 273 = 102°C.

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18.35 *Estimate the temperature at which GaAs has an electrical conductivity of 3.7 3 10^{23} (V-m)^{21} assuming the temperature dependence for σ of Equation 18.36. The data shown in Table 18.3 might prove helpful.*

Solution

This problem asks that we estimate the temperature at which GaAs has an electrical conductivity of 3.7×10^{-3} $(\Omega\text{-m})^{-1}$ assuming that the conductivity has a temperature dependence as shown in Equation 18.36. From the room temperature (298 K) conductivity [10^{-6} $(\Omega\text{-m})^{-1}$] and band gap energy (1.42 eV) of Table 18.3 we determine the value of C (Equation 18.36) by taking natural logarithms of both sides of the equation, and after rearrangement as follows:

$$\ln C = \ln \sigma + \frac{3}{2}\ln T + \frac{E_g}{2kT}$$

$$= \ln \left[10^{-6}\ (\Omega - \text{m})^{-1}\right] + \frac{3}{2}\ln\ (298\ \text{K}) + \frac{1.42\ \text{eV}}{(2)(8.62 \times 10^{-5}\ \text{eV/K})(298\ \text{K})}$$

$$= 22.37$$

Now we substitute this value into Equation 18.36 in order to determine the value of T for which $\sigma = 3.7 \times 10^{-3}$ $(\Omega\text{-m})^{-1}$, thus

$$\ln \sigma = \ln C - \frac{3}{2}\ln T - \frac{E_g}{2kT}$$

$$\ln \left[3.7 \times 10^{-3}\ (\Omega\text{-m})^{-1}\right] = 22.37 - \frac{3}{2}\ln T - \frac{1.42\ \text{eV}}{(2)(8.62 \times 10^{-5}\ \text{eV/K})(T)}$$

This equation may be solved for T using an equation solver. For some solvers, the following set of instructions may be used:

$$\ln(3.7*10\text{^}{-3}) = 22.37 - 1.5*\ln(T) - 1.42/(2*8.62*10\text{^}{-5}*T)$$

The resulting solution is $T = 437$; this value is the temperature in K which corresponds to T(ºC) = 437 K – 273 = 164°C.

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18.36 *Compare the temperature dependence of the conductivity for metals and intrinsic semiconductors. Briefly explain the difference in behavior.*

Solution

For metals, the temperature dependence is described by Equation 18.10 (and converting from resistivity to conductivity using Equation 18.4), as

$$\sigma = \frac{1}{\rho_0 + aT}$$

That is, the electrical conductivity decreases with increasing temperature.

Alternatively, from Equation 18.8, the conductivity of metals is equal to

$$\sigma = n|e|\mu_e$$

As the temperature rises, n will remain virtually constant, whereas the mobility (μ_e) will decrease, because the thermal scattering of free electrons will become more efficient. Since $|e|$ is independent of temperature, the net result will be diminishment in the magnitude of σ.

For intrinsic semiconductors, the temperature-dependence of conductivity is just the opposite of that for metals—i.e, conductivity increases with rising temperature. One explanation is as follows: Equation 18.15 describes the conductivity; i.e.,

$$\sigma = n|e|(\mu_e + \mu_h) = p|e|(\mu_e + \mu_h)$$
$$= n_i|e|(\mu_e + \mu_h)$$

Both n and p increase dramatically with rising temperature (Figure 18.16), since more thermal energy becomes available for valence band-conduction band electron excitations. The magnitudes of μ_e and μ_h will diminish somewhat with increasing temperature (per the upper curves of Figures 18.19a and 18.19b), as a consequence of the thermal scattering of electrons and holes. However, this reduction of μ_e and μ_h will be overwhelmed by the increase in n and p, with the net result is that σ increases with temperature.

An alternative explanation is as follows: for an intrinsic semiconductor the temperature dependence is represented by an equation of the form of Equation 18.36. This expression contains two terms that involve temperature—a preexponential one (in this case $T^{-3/2}$) and the other in the exponential. With rising temperature the preexponential term decreases, while the exp ($-E_g/2kT$) parameter increases. With regard to relative magnitudes,

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the exponential term increases much more rapidly than the preexponential one, such that the electrical conductivity of an intrinsic semiconductor increases with rising temperature.

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Factors That Affect Carrier Mobility

18.37 *Calculate the room-temperature electrical conductivity of silicon that has been doped with* 5×10^{22} m^{-3} *of boron atoms.*

Solution

This problems asks that we determine the room-temperature electrical conductivity of silicon that has been doped with 5×10^{22} m^{-3} of boron atoms. Inasmuch as B is a group IIIA element in the periodic table (Figure 2.6) it acts as an acceptor in silicon. Thus, this material is *p*-type extrinsic, and it is necessary to use Equation 18.17, with $p = 5 \times 10^{22}$ m^{-3} since at room temperature all of the B acceptor impurities are ionized. The hole mobility, from Figure 18.18 at an impurity concentration of 5×10^{22} m^{-3}, is 0.028 m^2/V-s. Therefore, the conductivity is equal to

$$\sigma = p\,|e|\,\mu_h = (5 \times 10^{22}\ \text{m}^{-3})(1.602 \times 10^{-19}\ \text{C})(0.028\ \text{m}^2/\text{V}-\text{s}) = 224\ (\Omega - \text{m})^{-1}$$

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18.38 *Calculate the room-temperature electrical conductivity of silicon that has been doped with* 2×10^{23} m^{-3} *of arsenic atoms.*

Solution

Here we are asked to calculate the room-temperature electrical conductivity of silicon that has been doped with 2×10^{23} m^{-3} of arsenic atoms. Inasmuch as As is a group VA element in the periodic table (Figure 2.6) it acts as a donor in silicon. Thus, this material is *n*-type extrinsic, and it is necessary to use Equation 18.16, with $n = 2 \times 10^{23}$ m^{-3} since at room temperature all of the As donor impurities are ionized. The electron mobility, from Figure 18.18 at an impurity concentration of 2×10^{23} m^{-3}, is 0.05 m^2/V-s. Therefore, the conductivity is equal to

$$\sigma = n|e|\mu_e = (2 \times 10^{23}\ \text{m}^{-3})(1.602 \times 10^{-19}\ \text{C})(0.05\ \text{m}^2/\text{V}-\text{s}) = 1600\ (\Omega - \text{m})^{-1}$$

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18.39 *Estimate the electrical conductivity, at 125°C, of silicon that has been doped with 10^{23} m^{-3} of aluminum atoms.*

Solution

In this problem we are to estimate the electrical conductivity, at 125°C, of silicon that has been doped with 10^{23} m^{-3} of aluminum atoms. Inasmuch as Al is a group IIIA element in the periodic table (Figure 2.6) it acts as an acceptor in silicon. Thus, this material is *p*-type extrinsic, and it is necessary to use Equation 18.17; p in this expression is 10^{23} m^{-3} since at 125°C all of the Al acceptor impurities are ionized. The hole mobility is determined using Figure 18.19*b*. From the 10^{23} m^{-3} impurity concentration curve and at 125°C (398 K), μ_h = 0.017 m^2/V-s. Therefore, the conductivity is equal to

$$\sigma = p\,|e|\,\mu_h = (10^{23}\ \text{m}^{-3})(1.602 \times 10^{-19}\ \text{C})(0.017\ \text{m}^2/\text{V}-\text{s}) = 272\ (\Omega - \text{m})^{-1}$$

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18.40 *Estimate the electrical conductivity, at 85°C, of silicon that has been doped with 10^{20} m^{-3} of phosphorus atoms.*

Solution

In this problem we are to estimate the electrical conductivity, at 85°C, of silicon that has been doped with 10^{20} m^{-3} of phosphorus atoms. Inasmuch as P is a group VA element in the periodic table (Figure 2.6) it acts as a donor in silicon. Thus, this material is *n*-type extrinsic, and it is necessary to use Equation 18.16; n in this expression is 10^{20} m^{-3} since at 85°C all of the P donor impurities are ionized. The electron mobility is determined using Figure 18.19*a*. From the $<10^{20}$ m^{-3} impurity concentration curve and at 85°C (358 K,) μ_e = 0.1 m^2/V-s. Therefore, the conductivity is equal to

$$\sigma = n\,|\,e\,|\,\mu_e = \left(10^{20}\ \text{m}^{-3}\right)\left(1.602 \times 10^{-19}\ \text{C}\right)\left(0.1\ \text{m}^2/\text{V}-\text{s}\right) = 1.6\ \ (\Omega - \text{m})^{-1}$$

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The Hall Effect

18.41 *Some hypothetical metal is known to have an electrical resistivity of 4×10^{-8} (Ω-m). Through a specimen of this metal that is 25 mm thick is passed a current of 30 A; when a magnetic field of 0.75 tesla is simultaneously imposed in a direction perpendicular to that of the current, a Hall voltage of -1.26×10^{-7} V is measured. Compute (a) the electron mobility for this metal, and (b) the number of free electrons per cubic meter.*

Solution

(a) This portion of the problem calls for us to determine the electron mobility for some hypothetical metal using the Hall effect. This metal has an electrical resistivity of 4×10^{-8} (Ω-m), while the specimen thickness is 25 mm, $I_x = 30$ A and $B_z = 0.75$ tesla; under these circumstances a Hall voltage of -1.26×10^{-7} V is measured. It is first necessary to convert resistivity to conductivity (Equation 18.4). Thus

$$\sigma = \frac{1}{\rho} = \frac{1}{4 \times 10^{-8}\ (\Omega - \text{m})} = 2.5 \times 10^{7}\ (\Omega - \text{m})^{-1}$$

The electron mobility may be determined using Equation 18.20b; and upon incorporation of Equation 18.18, we have

$$\mu_e = |R_H|\sigma$$

$$= \frac{|V_H|d\sigma}{I_x B_z}$$

$$= \frac{\left(\left|-1.26 \times 10^{-7}\ \text{V}\right|\right)(25 \times 10^{-3}\ \text{m})\left[2.5 \times 10^{7}\ (\Omega - \text{m})^{-1}\right]}{(30\ \text{A})(0.75\ \text{tesla})}$$

$$= 0.0035\ \text{m}^2/\text{V-s}$$

(b) Now we are to calculate the number of free electrons per cubic meter. From Equation 18.8 we have

$$n = \frac{\sigma}{|e|\mu_e}$$

$$= \frac{2.5 \times 10^{7}\ (\Omega - \text{m})^{-1}}{(1.602 \times 10^{-19}\ \text{C})(0.0035\ \text{m}^2/\text{V-s})}$$

$$= 4.46 \times 10^{28}\ \text{m}^{-3}$$

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18.42 *Some metal alloy is known to have electrical conductivity and electron mobility values of* 1.5×10^7 $(\Omega\text{-m})^{-1}$ *and* $0.0020\ m^2/V\text{-s}$, *respectively. Through a specimen of this alloy that is 35 mm thick is passed a current of 45 A. What magnetic field would need to be imposed to yield a Hall voltage of* -1.0×10^{-7} *V?*

Solution

In this problem we are asked to determine the magnetic field required to produce a Hall voltage of -1.0×10^{-7} V, given that $\sigma = 1.5 \times 10^7\ (\Omega\text{-m})^{-1}$, $\mu_e = 0.0020\ \text{m}^2/\text{V-s}$, $I_x = 45$ A, and $d = 35$ mm. Combining Equations 18.18 and 18.20b, and after solving for B_z, we get

$$B_z = \frac{|V_H|d}{I_x R_H} = \frac{|V_H|\sigma d}{I_x \mu_e}$$

$$= \frac{\left(\left|-1.0 \times 10^{-7}\ \text{V}\right|\right)\left[1.5 \times 10^7\ (\Omega - \text{m})^{-1}\right]\left(35 \times 10^{-3}\ \text{m}\right)}{(45\ \text{A})\left(0.0020\ \text{m}^2/\text{V-s}\right)}$$

$$= 0.58\ \text{tesla}$$

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Semiconducting Devices

18.43 *Briefly describe electron and hole motions in a p–n junction for forward and reverse biases; then explain how these lead to rectification.*

The explanations called for are found in Section 18.15.

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18.44 *How is the energy in the reaction described by Equation 18.21 dissipated?*

Solution

The energy generated by the electron-hole annihilation reaction, Equation 18.21, is dissipated as heat.

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18.45 *What are the two functions that a transistor may perform in an electronic circuit?*

Solution

In an electronic circuit, a transistor may be used to (1) amplify an electrical signal, and (2) act as a switching device in computers.

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18.46 *Cite the differences in operation and application for junction transistors and MOSFETs.*

The differences in operation and application for junction transistors and MOSFETs are described in Section 18.15.

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Conduction in Ionic Materials

18.47 *We noted in Section 12.5 (Figure 12.22) that in FeO (wüstite), the iron ions can exist in both Fe^{2+} and Fe^{3+} states. The number of each of these ion types depends on temperature and the ambient oxygen pressure. Furthermore, we also noted that in order to retain electroneutrality, one Fe^{2+} vacancy will be created for every two Fe^{3+} ions that are formed; consequently, in order to reflect the existence of these vacancies the formula for wüstite is often represented as $Fe_{(1-x)}O$ where x is some small fraction less than unity.*

In this nonstoichiometric $Fe_{(1-x)}O$ material, conduction is electronic, and, in fact, it behaves as a p-type semiconductor. That is, the Fe^{3+} ions act as electron acceptors, and it is relatively easy to excite an electron from the valence band into an Fe^{3+} acceptor state, with the formation of a hole. Determine the electrical conductivity of a specimen of wüstite that has a hole mobility of 1.0×10^{-5} m^2/V-s and for which the value of x is 0.060. Assume that the acceptor states are saturated (i.e., one hole exists for every Fe^{3+} ion). Wüstite has the sodium chloride crystal structure with a unit cell edge length of 0.437 nm.

Solution

We are asked in this problem to determine the electrical conductivity for the nonstoichiometric $Fe_{(1-x)}O$, given $x = 0.060$ and that the hole mobility is 1.0×10^{-5} m^2/V-s. It is first necessary to compute the number of vacancies per cubic meter for this material. For this determination let us use as our basis 10 unit cells. For the sodium chloride crystal structure there are four cations and four anions per unit cell. Thus, in ten unit cells of FeO there will normally be forty O^{2-} and forty Fe^{2+} ions. However, when $x = 0.06$, (0.06)(40) = 2.4 of the Fe^{2+} sites will be vacant. (Furthermore, there will be 4.8 Fe^{3+} ions in these ten unit cells inasmuch as two Fe^{3+} ions are created for every vacancy). Therefore, each unit cell will, on the average contain 0.24 vacancies. Now, the number of vacancies per cubic meter is just the number of vacancies per unit cell divided by the unit cell volume; this volume is just the unit cell edge length (0.437 nm) cubed. Thus

$$\frac{\#\text{ vacancies}}{\text{m}^3} = \frac{0.24\text{ vacancies/unit cell}}{(0.437 \times 10^{-9}\text{ m})^3}$$

$$= 2.88 \times 10^{27}\text{ vacancies/m}^3$$

Inasmuch as it is assumed that the vacancies are saturated, the number of holes (p) is also 2.88×10^{27} m^{-3}. It is now possible, using Equation 18.17, to compute the electrical conductivity of this material as

$$\sigma = p|e|\mu_h$$

$$= (2.88 \times 10^{27}\text{ m}^{-3})(1.602 \times 10^{-19}\text{ C})(1.0 \times 10^{-5}\text{ m}^2/\text{V-s}) = 4613\ (\Omega\text{-m})^{-1}$$

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18.48 *At temperatures between 775°C (1048 K) and 1100°C (1373 K), the activation energy and preexponential for the diffusion coefficient of Fe^{2+} in FeO are 102,000 J/mol and 7.3 × 10^{-8} m^2/s, respectively. Compute the mobility for an Fe^{2+} ion at 1000°C (1273 K).*

Solution

For this problem, we are given, for FeO, the activation energy (102,000 J/mol) and preexponential (7.3 × 10^{-8} m^2/s) for the diffusion coefficient of Fe^{2+} and are asked to compute the mobility for a Fe^{2+} ion at 1273 K. The mobility, $\mu_{Fe^{2+}}$, may be computed using Equation 18.23; however, this expression also includes the diffusion coefficient $D_{Fe^{2+}}$, which is determined using Equation 5.8 as

$$D_{Fe^{2+}} = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$$= \left(7.3 \times 10^{-8}\ \text{m}^2/\text{s}\right) \exp\left[-\frac{102{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1273\ \text{K})}\right]$$

$$= 4.74 \times 10^{-12}\ \text{m}^2/\text{s}$$

Now solving for $\mu_{Fe^{2+}}$ yields

$$\mu_{Fe^{2+}} = \frac{n_{Fe^{2+}} e D_{Fe^{2+}}}{kT}$$

$$= \frac{(2)\left(1.602 \times 10^{-19}\ \text{C/atom}\right)\left(4.74 \times 10^{-12}\ \text{m}^2/\text{s}\right)}{\left(1.38 \times 10^{-23}\ \text{J/atom-K}\right)(1273\ \text{K})}$$

$$= 8.64 \times 10^{-11}\ \text{m}^2/\text{V-s}$$

(Note: the value of $n_{Fe^{2+}}$ is two, inasmuch as two electrons are involved in the ionization of Fe to Fe^{2+}.)

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Capacitance

18.49 *A parallel-plate capacitor using a dielectric material having an ε_r of 2.5 has a plate spacing of 1 mm (0.04 in.). If another material having a dielectric constant of 4.0 is used and the capacitance is to be unchanged, what must be the new spacing between the plates?*

Solution

We want to compute the plate spacing of a parallel-plate capacitor as the dielectric constant is increased form 2.5 to 4.0, while maintaining the capacitance constant. Combining Equations 18.26 and 18.27 yields

$$C = \frac{\varepsilon A}{l} = \frac{\varepsilon_r \varepsilon_0 A}{l}$$

Now, let us use the subscripts 1 and 2 to denote the initial and final states, respectively. Since $C_1 = C_2$, then

$$\frac{\varepsilon_{r1} \varepsilon_0 A}{l_1} = \frac{\varepsilon_{r2} \varepsilon_0 A}{l_2}$$

And, solving for l_2

$$l_2 = \frac{\varepsilon_{r2} l_1}{\varepsilon_{r1}} = \frac{(4.0)(1 \text{ mm})}{2.5} = 1.6 \text{ mm}$$

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18.50 *A parallel-plate capacitor with dimensions of 100 mm by 25 mm and a plate separation of 3 mm must have a minimum capacitance of 38 pF (3.8×10^{-11} F) when an ac potential of 500 V is applied at a frequency of 1 MHz. Which of those materials listed in Table 18.5 are possible candidates? Why?*

Solution

This problem asks for us to ascertain which of the materials listed in Table 18.5 are candidates for a parallel-plate capacitor that has dimensions of 100 mm by 25 mm, a plate separation of 3 mm so as to have a minimum capacitance of 3.8×10^{-11} F, when an ac potential of 500 V is applied at 1 MHz. Upon combining Equations 18.26 and 18.27 and solving for the dielectric constant ε_r we get

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} = \frac{lC}{\varepsilon_0 A}$$

$$= \frac{(3 \times 10^{-3}\,\text{m})(3.8 \times 10^{-11}\,\text{F})}{(8.85 \times 10^{-12}\,\text{F/m})(100 \times 10^{-3}\,\text{m})(25 \times 10^{-3}\,\text{m})}$$

$$= 5.15$$

Thus, the minimum value of ε_r to achieve the desired capacitance is 5.15 at 1 MHz. Of those materials listed in the table, titanate ceramics, mica, steatite, soda-lime glass, and porcelain are candidates.

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18.51 *Consider a parallel-plate capacitor having an area of 2500 mm^2 and a plate separation of 2 mm, and with a material of dielectric constant 4.0 positioned between the plates. (a) What is the capacitance of this capacitor? (b) Compute the electric field that must be applied for 8.0 × 10^{-9} C to be stored on each plate.*

Solution

In this problem we are given, for a parallel-plate capacitor, its area (2500 mm^2), the plate separation (2 mm), and that a material having an ε_r of 4.0 is positioned between the plates.

(a) We are first asked to compute the capacitance. Combining Equations 18.26 and 18.27, and solving for C yields

$$C = \frac{\varepsilon A}{l} = \frac{\varepsilon_r \varepsilon_0 A}{l}$$

$$= \frac{(4.0)(8.85 \times 10^{-12}\ \text{F/m})(2500\ \text{mm}^2)(1\ \text{m}^2/10^6\ \text{mm}^2)}{2 \times 10^{-3}\ \text{m}}$$

$$= 4.43 \times 10^{-11}\ \text{F} = 44.3\ \text{pF}$$

(b) Now we are asked to compute the electric field that must be applied in order that 8 × 10^{-9} C be stored on each plate. First we need to solve for V in Equation 18.24 as

$$V = \frac{Q}{C} = \frac{8 \times 10^{-9}\ \text{C}}{4.43 \times 10^{-11}\ \text{F}} = 181\ \text{V}$$

The electric field E may now be determined using Equation 18.6; thus

$$E = \frac{V}{l} = \frac{181\ \text{V}}{2 \times 10^{-3}\ \text{m}} = 9.1 \times 10^4\ \text{V/m}$$

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18.52 *In your own words, explain the mechanism by which charge storing capacity is increased by the insertion of a dielectric material within the plates of a capacitor.*

This explanation is found in Section 18.19.

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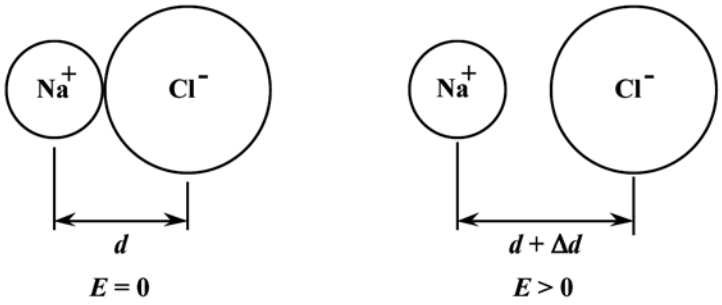
Field Vectors and Polarization

Types of Polarization

18.53 *For NaCl, the ionic radii for Na^+ and Cl^- ions are 0.102 and 0.181 nm, respectively. If an externally applied electric field produces a 5% expansion of the lattice, compute the dipole moment for each Na^+–Cl^- pair. Assume that this material is completely unpolarized in the absence of an electric field.*

Solution

Shown below are the relative positions of Na^+ and Cl^- ions, without and with an electric field present.



Now,

$$d = r_{Na^+} + r_{Cl^-} = 0.102 \text{ nm} + 0.181 \text{ nm} = 0.283 \text{ nm}$$

and

$$\Delta d = 0.05\, d = (0.05)(0.283 \text{ nm}) = 0.0142 \text{ nm} = 1.42 \times 10^{-11} \text{ m}$$

From Equation 18.28, the dipole moment, p, is just

$$p = q\,\Delta d$$

$$= (1.602 \times 10^{-19} \text{ C})(1.42 \times 10^{-11} \text{ m})$$

$$= 2.26 \times 10^{-30} \text{ C-m}$$

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18.54 *The polarization P of a dielectric material positioned within a parallel-plate capacitor is to be 1.0 × 10^{-6} C/m^2.*

(a) What must be the dielectric constant if an electric field of 5 × 10^4 V/m is applied?

(b) What will be the dielectric displacement D?

Solution

(a) In order to solve for the dielectric constant in this problem, we must employ Equation 18.32, in which the polarization and the electric field are given. Solving for ε_r from this expression gives

$$\varepsilon_r = \frac{P}{\varepsilon_0 E} + 1$$

$$= \frac{1.0 \times 10^{-6}\ \text{C/m}^2}{(8.85 \times 10^{-12}\ \text{F/m})(5 \times 10^4\ \text{V/m})} + 1$$

$$= 3.26$$

(b) The dielectric displacement may be determined using Equation 18.31, as

$$D = \varepsilon_0 E + P$$

$$= (8.85 \times 10^{-12}\ \text{F/m})(5 \times 10^4\ \text{V/m}) + 1.0 \times 10^{-6}\ \text{C/m}^2$$

$$= 1.44 \times 10^{-6}\ \text{C/m}^2$$

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18.55 *A charge of 3.5 × 10^{-11} C is to be stored on each plate of a parallel-plate capacitor having an area of 160 mm^2 (0.25 in.^{2}) and a plate separation of 3.5 mm (0.14 in.).*

(a) What voltage is required if a material having a dielectric constant of 5.0 is positioned within the plates?

(b) What voltage would be required if a vacuum were used?

(c) What are the capacitances for parts (a) and (b)?

(d) Compute the dielectric displacement for part (a).

(e) Compute the polarization for part (a).

Solution

(a) We want to solve for the voltage when $Q = 3.5 \times 10^{-11}$ C, $A = 160$ mm^2, $l = 3.5$ mm, and $\varepsilon_r = 5.0$. Combining Equations 18.24, 18.26, and 18.27 yields

$$C = \frac{Q}{V} = \varepsilon \frac{A}{l} = \varepsilon_r \varepsilon_0 \frac{A}{l}$$

Or

$$\frac{Q}{V} = \varepsilon_r \varepsilon_0 \frac{A}{l}$$

And, solving for V, and incorporating values provided in the problem statement, leads to

$$V = \frac{Q l}{\varepsilon_r \varepsilon_0 A}$$

$$= \frac{(3.5 \times 10^{-11}\ \text{C})(3.5 \times 10^{-3}\ \text{m})}{(5.0)(8.85 \times 10^{-12}\ \text{F/m})(160\ \text{mm}^2)(1\ \text{m}^2/10^6\ \text{mm}^2)}$$

$$= 17.3\ \text{V}$$

(b) For this same capacitor, if a vacuum is used

$$V = \frac{Q l}{\varepsilon_0 A}$$

$$= \frac{(3.5 \times 10^{-11}\ \text{C})(3.5 \times 10^{-3}\ \text{m})}{(8.85 \times 10^{-12}\ \text{F/m})(160 \times 10^{-6}\ \text{m}^2)}$$

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$$= 86.5 \text{ V}$$

(c) The capacitance for part (a) is just

$$C = \frac{Q}{V} = \frac{3.5 \times 10^{-11} \text{ C}}{17.3 \text{ V}} = 2.0 \times 10^{-12} \text{ F}$$

While for part (b)

$$C = \frac{Q}{V} = \frac{3.5 \times 10^{-11} \text{ C}}{86.5 \text{ V}} = 4.0 \times 10^{-13} \text{ F}$$

(d) The dielectric displacement may be computed by combining Equations 18.31, 18.32 and 18.6, as

$$D = \varepsilon_0 E + P = \varepsilon_0 E + \varepsilon_0(\varepsilon_r - 1)E = \varepsilon_0 \varepsilon_r E = \frac{\varepsilon_0 \varepsilon_r V}{l}$$

And incorporating values for ε_r and l provided in the problem statement, as well as the value of V computed in part (a)

$$D = \frac{(8.85 \times 10^{-12} \text{ F/m})(5.0)(17.3 \text{ V})}{3.5 \times 10^{-3} \text{ m}}$$

$$= 2.2 \times 10^{-7} \text{ C/m}^2$$

(e) The polarization is determined using Equations 18.32 and 18.6 as

$$P = \varepsilon_0(\varepsilon_r - 1)E = \varepsilon_0(\varepsilon_r - 1)\frac{V}{l}$$

$$= \frac{(8.85 \times 10^{-12} \text{ F/m})(5.0 - 1)(17.3 \text{ V})}{3.5 \times 10^{-3} \text{ m}}$$

$$= 1.75 \times 10^{-7} \text{ C/m}^2$$

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18.56 *(a) For each of the three types of polarization, briefly describe the mechanism by which dipoles are induced and/or oriented by the action of an applied electric field. (b) For solid lead titanate ($PbTiO_3$), gaseous neon, diamond, solid KCl, and liquid NH_3 what kind(s) of polarization is (are) possible? Why?*

Solution

(a) For electronic polarization, the electric field causes a net displacement of the center of the negatively charged electron cloud relative to the positive nucleus. With ionic polarization, the cations and anions are displaced in opposite directions as a result of the application of an electric field. Orientation polarization is found in substances that possess permanent dipole moments; these dipole moments become aligned in the direction of the electric field.

(b) Electronic, ionic, and orientation polarizations would be observed in lead titanate. The lead, titanium, and oxygen would undoubtedly be largely ionic in character. Furthermore, orientation polarization is also possible inasmuch as permanent dipole moments may be induced in the same manner as for $BaTiO_3$ as shown in Figure 18.35.

Only electronic polarization is to be found in gaseous neon; being an inert gas, its atoms will not be ionized nor possess permanent dipole moments.

Only electronic polarization is to be found in solid diamond; this material does not have molecules with permanent dipole moments, nor is it an ionic material.

Both electronic and ionic polarizations will be found in solid KCl, since it is strongly ionic. In all probability, no permanent dipole moments will be found in this material.

Both electronic and orientation polarizations are found in liquid NH_3. The NH_3 molecules have permanent dipole moments that are easily oriented in the liquid state.

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18.57 *(a) Compute the magnitude of the dipole moment associated with each unit cell of $BaTiO_3$, as illustrated in Figure 18.35.*

(b) Compute the maximum polarization that is possible for this material.

Solution

(a) This portion of the problem asks that we compute the magnitude of the dipole moment associated with each unit cell of $BaTiO_3$, which is illustrated in Figure 18.35. The dipole moment p is defined by Equation 18.28 as $p = qd$ in which q is the magnitude of each dipole charge, and d is the distance of separation between the charges. Each Ti^{4+} ion has four units of charge associated with it, and thus $q = (4)(1.602 \times 10^{-19}\ \text{C}) = 6.41 \times 10^{-19}\ \text{C}$. Furthermore, d is the distance the Ti^{4+} ion has been displaced from the center of the unit cell, which is just 0.006 nm + 0.006 nm = 0.012 nm [Figure 18.35(b)]. Hence

$$p = qd = (6.41 \times 10^{-19}\ \text{C})(0.012 \times 10^{-9}\ \text{m})$$

$$= 7.69 \times 10^{-30}\ \text{C-m}$$

(b) Now it becomes necessary to compute the maximum polarization that is possible for this material. The maximum polarization will exist when the dipole moments of all unit cells are aligned in the same direction. Furthermore, it is computed by dividing the above value of p by the volume of each unit cell, which is equal to the product of three unit cell edge lengths, as shown in Figure 18.35. Thus

$$P = \frac{p}{V_C}$$

$$= \frac{7.69 \times 10^{-30}\ \text{C} - \text{m}}{(0.403 \times 10^{-9}\ \text{m})(0.398 \times 10^{-9}\ \text{m})(0.398 \times 10^{-9}\ \text{m})}$$

$$= 0.121\ \text{C/m}^2$$

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Frequency Dependence of the Dielectric Constant

18.58 *The dielectric constant for a soda–lime glass measured at very high frequencies (on the order of 10^{15} Hz) is approximately 2.3. What fraction of the dielectric constant at relatively low frequencies (1 MHz) is attributed to ionic polarization? Neglect any orientation polarization contributions.*

Solution

For this soda-lime glass, in order to compute the fraction of the dielectric constant at low frequencies that is attributed to ionic polarization, we must determine the ε_r within this low-frequency regime; such is tabulated in Table 18.5, and at 1 MHz its value is 6.9. Thus, this fraction is just

$$\text{fraction} = \frac{\varepsilon_r(\text{low}) - \varepsilon_r(\text{high})}{\varepsilon_r(\text{low})}$$

$$= \frac{6.9 - 2.3}{6.9} = 0.67$$

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Ferroelectricity

18.59 *Briefly explain why the ferroelectric behavior of $BaTiO_3$ ceases above its ferroelectric Curie temperature.*

Solution

The ferroelectric behavior of $BaTiO_3$ ceases above its ferroelectric Curie temperature because the unit cell transforms from tetragonal geometry to cubic; thus, the Ti^{4+} is situated at the center of the cubic unit cell, there is no charge separation, and no net dipole moment.

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DESIGN PROBLEMS

Electrical Resistivity of Metals

18.D1 *A 95 wt% Pt-5 wt% Ni alloy is known to have an electrical resistivity of 2.35 × 10^{-7} Ω-m at room temperature (25°C). Calculate the composition of a platinum-nickel alloy that gives a room-temperature resistivity of 1.75 × 10^{-7} Ω-m. The room-temperature resistivity of pure platinum may be determined from the data in Table 18.1; assume that platinum and nickel form a solid solution.*

Solution

This problem asks that we calculate the composition of a platinum-nickel alloy that has a room temperature resistivity of 1.75 × 10^{-7} Ω-m. The first thing to do is, using the 95 Pt-5 Ni resistivity data, determine the impurity contribution, and, from this result, calculate the constant A in Equation 18.11. Thus,

$$\rho_{total} = 2.35 \times 10^{-7}\ (\Omega\text{-m}) = \rho_i + \rho_t$$

From Table 18.1, for pure platinum, and using Equation 18.4

$$\rho_t = \frac{1}{\sigma} = \frac{1}{0.94 \times 10^7\ (\Omega - \text{m})^{-1}} = 1.064 \times 10^{-7}\ (\Omega\text{-m})$$

Thus, for the 95 Pt-5 Ni alloy

$$\rho_i = \rho_{total} - \rho_t = 2.35 \times 10^{-7} - 1.064 \times 10^{-7}$$

$$= 1.286 \times 10^{-7}\ (\Omega\text{-m})$$

In the problem statement, the impurity (i.e., nickel) concentration is expressed in weight percent. However, Equation 18.11 calls for concentration in atom fraction (i.e., atom percent divided by 100). Consequently, conversion from weight percent to atom fraction is necessary. (Note: we now choose to denote the atom fraction of nickel as c'_{Ni}, and the weight percents of Ni and Pt by C_{Ni} and C_{Pt}, respectively.) Using these notations, this conversion may be accomplished by using a modified form of Equation 4.6a as

$$c'_{Ni} = \frac{C'_{Ni}}{100} = \frac{C_{Ni} A_{Pt}}{C_{Ni} A_{Pt} + C_{Pt} A_{Ni}}$$

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Here A_{Ni} and A_{Pt} denote the atomic weights of nickel and platinum (which values are 58.69 and 195.08 g/mol, respectively). Thus

$$c'_{Ni} = \frac{(5\ \text{wt\%})(195.08\ \text{g/mol})}{(5\ \text{wt\%})(195.08\ \text{g/mol}) + (95\ \text{wt\%})(58.69\ \text{g/mol})}$$

$$= 0.15$$

Now, solving for A in Equation 18.11

$$A = \frac{\rho_i}{c'_{Ni}\left(1 - c'_{Ni}\right)}$$

$$= \frac{1.286 \times 10^{-7}\,(\Omega - \text{m})}{(0.15)(1 - 0.15)} = 1.01 \times 10^{-6}\ (\Omega\text{-m})$$

Now it is possible to compute the c'_{Ni} to give a room temperature resistivity of 1.75×10^{-7} Ω-m. Again, we must determine ρ_i as

$$\rho_i = \rho_{total} - \rho_t$$

$$= 1.75 \times 10^{-7} - 1.286 \times 10^{-7} = 4.64 \times 10^{-8}\ (\Omega\text{-m})$$

If Equation 18.11 is expanded, then

$$\rho_i = A c'_{Ni} - A c'^{2}_{Ni}$$

Or, rearranging this equation, we have

$$A c'^{2}_{Ni} - A c'_{Ni} + \rho_i = 0$$

Now, solving for c'_{Ni} (using the quadratic equation solution)

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$$c'_{\text{Ni}} = \frac{A \pm \sqrt{A^2 - 4A\rho_i}}{2A}$$

Again, from the above

$A = 1.01 \times 10^{-6}$ (Ω-m)
$\rho_i = 4.64 \times 10^{-8}$ (Ω-m)

which leads to

$$c'_{\text{Ni}} = \frac{1.01 \times 10^{-6} \pm \sqrt{(1.01 \times 10^{-6})^2 - (4)(1.01 \times 10^{-6})(4.64 \times 10^{-8})}}{(2)(1.01 \times 10^{-6})}$$

And, taking the negative root,

$$c'_{\text{Ni}} = 0.0483$$

Or, in terms of atom percent,

$$C_{\text{Ni}}\tilde{\mathbf{O}} = 100 c_{\text{Ni}}\tilde{\mathbf{O}} = (100)(0.0483) = 4.83 \text{ at\%}$$

While the concentration of platinum is

$$C_{\text{Pt}}\tilde{\mathbf{O}} = 100 - C_{\text{Ni}}\tilde{\mathbf{O}} = 100.00 - 4.83 = 95.17 \text{ at\%}$$

Now, converting this composition to weight percent Ni, requires that we use Equation 4.7a as

$$C_{\text{Ni}} = \frac{C'_{\text{Ni}} A_{\text{Ni}}}{C'_{\text{Ni}} A_{\text{Ni}} + C'_{\text{Pt}} A_{\text{PT}}} \times 100$$

$$= \frac{(4.83 \text{ at\%})(58.69 \text{ g/mol})}{(4.83 \text{ at\%})(58.69 \text{ g/mol}) + (95.17 \text{ at\%})(195.08 \text{ g/mol})} \times 100$$

$$= 1.50 \text{ wt\%}$$

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18.D2 *Using information contained in Figures 18.8 and 18.38, determine the electrical conductivity of an 80 wt% Cu-20 wt% Zn alloy at -150°C (-240°F).*

Solution

This problem asks that we determine the electrical conductivity of an 80 wt% Cu-20 wt% Zn alloy at –150°C using information contained in Figures 18.8 and 18.38. In order to solve this problem it is necessary to employ Equation 18.9 which is of the form

$$\rho_{total} = \rho_t + \rho_i$$

since it is assumed that the alloy is undeformed. Let us first determine the value of ρ_i at room temperature (25°C) which value will be independent of temperature. From Figure 18.8, at 25°C and for pure Cu, $\rho_t(25) = 1.75 \times 10^{-8}$ Ω-m. Now, since it is assumed that the curve in Figure 18.38 was generated also at room temperature, we may take ρ as $\rho_{total}(25)$ at 80 wt% Cu-20 wt% Zn which has a value of 5.3×10^{-8} Ω-m. Thus

$$\rho_i = \rho_{total}(25) - \rho_t(25)$$

$$= 5.3 \times 10^{-8}\ \Omega\text{-m} - 1.75 \times 10^{-8}\ \Omega\text{-m} = 3.55 \times 10^{-8}\ \Omega\text{-m}$$

Finally, we may determine the resistivity at –150°C, $\rho_{total}(-150)$, by taking the resistivity of pure Cu at –150°C from Figure 18.8, which gives us $\rho_t(-150) = 0.55 \times 10^{-8}$ Ω-m. Therefore

$$\rho_{total}(-150) = \rho_i + \rho_t(-150)$$

$$= 3.55 \times 10^{-8}\ \Omega\text{-m} + 0.55 \times 10^{-8}\ \Omega\text{-m} = 4.10 \times 10^{-8}\ \Omega\text{-m}$$

And, using Equation 18.4 the conductivity is calculated as

$$\sigma = \frac{1}{\rho} = \frac{1}{4.10 \times 10^{-8}\ \Omega - \text{m}} = 2.44 \times 10^{7}\ (\Omega\text{-m})^{-1}$$

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18.D3 *Is it possible to alloy copper with nickel to achieve a minimum tensile strength of 375 MPa (54,400 psi) and yet maintain an electrical conductivity of 2.5 × 10^6 $(\Omega\text{-m})^{-1}$? If not, why? If so, what concentration of nickel is required? You may want to consult Figure 7.16a.*

Solution

To solve this problem, we want to consult Figures 7.16*a* and 18.9 in order to determine the Ni concentration ranges over which the tensile strength is greater than 375 MPa (54,500 psi) and the conductivity exceeds 2.5 × 10^6 $(\Omega\text{-m})^{-1}$.

From Figure 7.16*a*, a Ni concentration greater than about 30 wt% is necessary for a tensile strength in excess of 375 MPa. In Figure 18.9 is plotted the resistivity versus the Ni content. Since conductivity is the reciprocal of resistivity, the resistivity must be less than 40 × 10^{-8} Ω-m--i.e., $\frac{1}{2.5 \times 10^6\ (\Omega - \text{m})^{-1}}$. According to the figure, this will be the case for Ni concentrations less than 32.5 wt%.

Hence, it *is possible* to prepare an alloy meeting the criteria. The concentration of Ni would have to lie between about 30 and 32.5 wt%.

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Extrinsic Semiconduction
Factors That Affect Carrier Mobility

18.D4 *Specify an acceptor impurity type and concentration (in weight percent) that will produce a p-type silicon material having a room temperature electrical conductivity of 50 $(\Omega\text{-m})^{-1}$.*

Solution

First of all, those elements which, when added to silicon render it *p*-type, lie one group to the left of silicon in the periodic table; these include the group IIIA elements (Figure 2.6)--i.e., boron, aluminum, gallium, and indium.

Since this material is extrinsic and *p*-type, $p >> n$, and the electrical conductivity is a function of the hole concentration according to Equation 18.17. Also, the number of holes is about equal to the number of acceptor impurities, N_a. That is

$$p \sim N_a$$

From Equation 18.17, the conductivity is a function of both the hole concentration (p) and the hole mobility (μ_h). Furthermore, the room-temperature hole mobility is dependent on impurity concentration (Figure 18.18). One way to solve this problem is to use an iterative approach—i.e., assume some acceptor impurity concentration (which will also equal the value of p), then determine a "calculated" hole mobility from Equation 18.17—i.e.,

$$\mu_h = \frac{\sigma}{p\,|e|}$$

and, finally, compare this mobility with the "measured" value from Figure 18.18, taken at the assumed p (i.e., N_a) value.

Let us begin by assuming that $N_a = 10^{22}\ \text{m}^{-3}$. Thus, the "calculated" mobility value is

$$\mu_h = \frac{\sigma}{p\,|e|} = \frac{50\ (\Omega - \text{m})^{-1}}{(10^{22}\ \text{m}^{-3})(1.602 \times 10^{-19}\ \text{C})} = 0.0312\ \text{m}^2/\text{V} - \text{s}$$

From Figure 18.18, at an impurity concentration of $10^{22}\ \text{m}^{-3}$ the "measured" hole mobility is 0.0362 m^2/V-s, which is slightly higher than the "calculated" value.

For our next choice, let us assume a lower impurity concentration, say $5 \times 10^{21}\ \text{m}^{-3}$. At this lower concentration there will be an increase of both "calculated" and "measured" electron mobilities. The "calculated" value is just

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$$\mu_h = \frac{\sigma}{p\,|e|} = \frac{50\ (\Omega - \text{m})^{-1}}{\left(5 \times 10^{21}\ \text{m}^{-3}\right)\left(1.602 \times 10^{-19}\ \text{C}\right)} = 0.0624\ \text{m}^2/\text{V}-\text{s}$$

Whereas, Figure 18.18 yields a "measured" μ_h of 0.0394 m^2/V-s, which is lower than the "calculated" value. Therefore, the correct impurity concentration will lie somewhere between 5×10^{21} and 10^{22} m^{-3} probably closer to the latter of these two values. At 8.0×10^{22} m^{-3}, both "measured" and "calculated" μ_h values are about equal (0.039 m^2/V-s).

It next becomes necessary to calculate the concentration of acceptor impurities in atom percent. This computation first requires the determination of the number of silicon atoms per cubic meter, N_{Si}, using Equation 4.2, which is as follows

$$N_{Si} = \frac{N_A \rho'_{Si}}{A_{Si}}$$

$$= \frac{\left(6.022 \times 10^{23}\ \text{atoms/mol}\right)\left(2.33\ \text{g/cm}^3\right)\left(10^6\ \text{cm}^3/\text{m}^3\right)}{28.09\ \text{g/mol}}$$

$$= 5.0 \times 10^{28}\ \text{m}^{-3}$$

(Note: in the above discussion, the density of silicon is represented by ρ'_{Si} in order to avoid confusion with resistivity, which is designated by ρ.)

The concentration of acceptor impurities in atom percent (C'_a) is just the ratio of N_a and $(N_a + N_{Si})$ multiplied by 100 as

$$C'_a = \frac{N_a}{N_a + N_{Si}} \times 100$$

$$= \frac{8.0 \times 10^{22}\ \text{m}^{-3}}{\left(8.0 \times 10^{22}\ \text{m}^{-3}\right) + \left(5.0 \times 10^{28}\ \text{m}^{-3}\right)} \times 100 = 1.6 \times 10^{-4}\ \text{at\%}$$

Now, conversion to weight percent (C_a) is possible using Equation 4.7a as

$$C_a = \frac{C'_a A_a}{C'_a A_a + C'_{Si} A_{Si}} \times 100$$

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where A_a and A_{Si} are the atomic weights of the acceptor and silicon, respectively. Thus, the concentration in weight percent will depend on the particular acceptor type. For example, for boron

$$C_B = \frac{C'_B A_B}{C'_B A_B + C'_{Si} A_{Si}} \times 100$$

$$= \frac{(1.6 \times 10^{-4}\ \text{at\%})(10.81\ \text{g/mol})}{(1.6 \times 10^{-4}\ \text{at\%})(10.81\ \text{g/mol}) + (99.99984\ \text{at\%})(28.09\ \text{g/mol})} \times 100$$

$$= 6.16 \times 10^{-5}\ \text{wt\%}$$

Similar calculations may be carried out for the other possible acceptor impurities which yield

$$C_{Al} = 1.54 \times 10^{-4}\ \text{wt\%}$$

$$C_{Ga} = 3.97 \times 10^{-4}\ \text{wt\%}$$

$$C_{In} = 6.54 \times 10^{-4}\ \text{wt\%}$$

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18.D5 *One integrated circuit design calls for diffusing boron into very high purity silicon at an elevated temperature. It is necessary that at a distance 0.2 μm from the surface of the silicon wafer, the room-temperature electrical conductivity be 1.2 × 10³ (Ω-m)⁻¹. The concentration of B at the surface of the Si is maintained at a constant level of 1.0 × 10²⁵ m⁻³; furthermore, it is assumed that the concentration of B in the original Si material is negligible, and that at room temperature the boron atoms are saturated. Specify the temperature at which this diffusion heat treatment is to take place if the treatment time is to be one hour. The diffusion coefficient for the diffusion of B in Si is a function of temperature as*

$$D(\text{m}^2/\text{s}) = 2.4 \times 10^{-4} \exp\left(-\frac{347 \text{ kJ/mol}}{RT}\right)$$

Solution

This problem asks for us to determine the temperature at which boron is to be diffused into high-purity silicon in order to achieve a room-temperature electrical conductivity of 1.2×10^3 $(\Omega\text{-m})^{-1}$ at a distance 0.2 μm from the surface if the B concentration at the surface is maintained at 1.0×10^{25} m^{-3}. It is first necessary for us to compute the hole concentration (since B is an acceptor in Si) at this 0.2 μm location.

From Equation 18.17, the conductivity is a function of both the hole concentration (p) and the hole mobility (μ_h). Furthermore, the room-temperature hole mobility is dependent on impurity concentration (Figure 18.18). One way to solve this problem is to use an iterative approach—i.e., assume some boron concentration, N_B (which will also equal the value of p), then determine a "calculated" hole mobility from Equation 18.17—i.e.,

$$\mu_h = \frac{\sigma}{p|e|}$$

and then compare this mobility with the "measured" value from Figure 18.18, taken at the assumed p (i.e., N_B).

Let us begin by assuming that $N_B = 10^{23}$ m^{-3}. Thus, the "calculated" mobility value is

$$\mu_h = \frac{\sigma}{p|e|} = \frac{1.2 \times 10^3 \ (\Omega - \text{m})^{-1}}{(10^{23} \ \text{m}^{-3})(1.602 \times 10^{-19} \ \text{C})} = 0.075 \ \text{m}^2/\text{V}-\text{s}$$

From Figure 18.18, at an impurity concentration of 10^{23} m^{-3} the "measured" hole mobility is 0.024 m^2/V-s, which is lower than the "calculated" value.

For our next choice, let us assume a higher boron concentration, say 10^{24} m^{-3}. At this higher concentration there will be a decrease of both "calculated" and "measured" hole mobilities. The "calculated" value is just

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$$\mu_h = \frac{\sigma}{p|e|} = \frac{1.2 \times 10^3 \ (\Omega - \text{m})^{-1}}{(10^{24} \ \text{m}^{-3})(1.602 \times 10^{-19} \ \text{C})} = 0.0075 \ \text{m}^2/\text{V} - \text{s}$$

Whereas, Figure 18.18 yields a "measured" μ_h of 0.01 m^2/V-s, which is lower than the "calculated" value. Therefore, the correct impurity concentration will lie somewhere between 10^{23} and 10^{24} m^{-3}. At 6.0×10^{23} m^{-3}, "measured" and "calculated" values are about equal (0.0125 m^2/V-s).

With regard to diffusion, the problem is one involving the nonsteady-state diffusion of B into the Si, wherein we have to solve for temperature. Temperature is incorporated into the diffusion coefficient expression given in the problem. But we must first employ the solution to Fick's second law for constant surface composition boundary conditions, Equation 5.5; in this expression C_0 is taken to be zero inasmuch as the problem stipulates that the initial boron concentration may be neglected. Thus,

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\frac{6.0 \times 10^{23} \ \text{m}^{-3} - 0}{1.0 \times 10^{25} \ \text{m}^{-3} - 0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

which reduces to

$$0.9400 = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

In order to solve this expression for a value $\frac{x}{2\sqrt{Dt}}$ of it is necessary to interpolate using data in Table 5.1. Thus

z	erf(z)
1.3	0.9340
z	0.9400
1.4	0.9523

$$\frac{z - 1.3}{1.4 - 1.3} = \frac{0.9400 - 0.9340}{0.9523 - 0.9340}$$

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From which, $z = 1.3328$; which is to say

$$1.3328 = \frac{x}{2\sqrt{Dt}}$$

Inasmuch as there are 3600 s/h (= t) and $x = 0.2\ \mu m$ (= 2×10^{-7} m) the above equation becomes

$$1.3328 = \frac{2 \times 10^{-7}\ \text{m}}{2\sqrt{(D)(3600\ \text{s})}}$$

which, when solving for the value of D, leads to

$$D = \frac{1}{3600\ \text{s}}\left[\frac{2 \times 10^{-7}\ \text{m}}{(2)(1.3328)}\right]^2 = 1.56 \times 10^{-18}\ \text{m}^2/\text{s}$$

Now, equating this value to the expression for D given in the problem gives

$$D = 1.56 \times 10^{-18}\ \text{m}^2/\text{s} = \left(2.4 \times 10^{-4}\right)\exp\left[-\frac{347{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(T)}\right]$$

To solve for T, let us take the natural logarithms of both sides of the above equation; this leads to

$$\ln\left(1.56 \times 10^{-18}\right) = \ln\left(2.4 \times 10^{-4}\right) - \frac{347{,}000}{8.31T}$$

$$-41.002 = -8.335 - \frac{4.176 \times 10^4}{T}$$

which yields a value for T of 1278 K (1005°C).

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Conduction in Ionic Materials

18.D6 *Problem 18.47 noted that FeO (wüstite) may behave as a semiconductor by virtue of the transformation of Fe^{2+} to Fe^{3+} and the creation of Fe^{2+} vacancies; the maintenance of electroneutrality requires that for every two Fe^{3+} ions, one vacancy is formed. The existence of these vacancies is reflected in the chemical formula of this nonstoichiometric wüstite as $Fe_{(1-x)}O$, where x is a small number having a value less than unity. The degree of nonstoichiometry (i.e., the value of x) may be varied by changing temperature and oxygen partial pressure. Compute the value of x that is required to produce an $Fe_{(1-x)}O$ material having a p-type electrical conductivity of 2000 $(\Omega\text{-m})^{-1}$; assume that the hole mobility is 1.0 × 10^{-5} m^2/V-s, the crystal structure for FeO is sodium chloride (with a unit cell edge length of 0.437 nm), and that the acceptor states are saturated.*

Solution

This problem asks, for the nonstoichiometric $Fe_{(1-x)}O$, given the electrical conductivity [2000 $(\Omega\text{-m})^{-1}$] and hole mobility (1.0 × 10^{-5} m^2/V-s) that we determine the value of x. It is first necessary to compute the number of holes per unit volume (p) using Equation 18.17. Thus

$$p = \frac{\sigma}{|e|\mu_h}$$

$$= \frac{2000\ (\Omega - \text{m})^{-1}}{(1.602 \times 10^{-19}\ \text{C})(1.0 \times 10^{-5}\ \text{m}^2/\text{V-s})} = 1.25 \times 10^{27}\ \text{holes/m}^3$$

Inasmuch as it is assumed that the acceptor states are saturated, the number of vacancies is also 1.25 × 10^{27} m^{-3}. Next, it is possible to compute the number of vacancies per unit cell by taking the product of the number of vacancies per cubic meter times the volume of a unit cell. This volume is just the unit cell edge length (0.437 nm) cubed:

$$\frac{\#\ \text{vacancies}}{\text{unit cell}} = (1.25 \times 10^{27}\ \text{m}^{-3})(0.437 \times 10^{-9}\ \text{m})^3 = 0.10$$

A unit cell for the sodium chloride structure contains the equivalence of four cations and four anions. Thus, if we take as a basis for this problem 10 unit cells, there will be one vacancy, 40 O^{2-} ions, and 39 iron ions (since one of the iron sites is vacant). (It should also be noted that since two Fe^{3+} ions are created for each vacancy, that of the 39 iron ions, 37 of them are Fe^{2+} and 2 of them are Fe^{3+}). In order to find the value of $(1 - x)$ in the chemical formula, we just take the ratio of the number of total Fe ions (39) and the number of total Fe ion sites (40). Thus

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$$(1 - x) = \frac{39}{40} = 0.975$$

Or the formula for this nonstoichiometric material is $Fe_{0.975}O$.

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Semiconductor Devices

18.D7 *One of the procedures in the production of integrated circuits is the formation of a thin insulating layer of SiO_2 on the surface of chips (see Figure 18.26). This is accomplished by oxidizing the surface of the silicon by subjecting it to an oxidizing atmosphere (i.e., gaseous oxygen or water vapor) at an elevated temperature. The rate of growth of the oxide film is parabolic—that is, the thickness of the oxide layer (x) is a function of time (t) according to the following equation:*

$$x^2 = Bt \qquad (18.37)$$

Here the parameter B is dependent on both temperature and the oxidizing atmosphere.

(a) For an atmosphere of O_2 at a pressure of 1 atm, the temperature dependence of B (in units of $\mu m^2/h$) is as follows:

$$B = 800 \exp\left(-\frac{1.24\ \text{eV}}{kT}\right) \qquad (18.38a)$$

where k is Boltmann's constant (8.62×10^{-5} eV/atom) and T is in K. Calculate the time required to grow an oxide layer (in an atmosphere of O_2) that is 75 nm thick at both 750°C and 900°C.

(b) In an atmosphere of H_2O (1 atm pressure), the expression for B (again in units of $\mu m^2/h$) is

$$B = 215 \exp\left(-\frac{0.70\ \text{eV}}{kT}\right) \qquad (18.38b)$$

Now calculate the time required to grow an oxide layer that is 75 nm thick (in an atmosphere of H_2O) at both 750°C and 900°C, and compare these times with those computed in part (a).

Solution

(a) In this portion of the problem we are asked to determine the time required to grow a layer of SiO_2 that is 75 nm (i.e., 0.075 μm) thick on the surface of a silicon chip at 900°C, in an atmosphere of O_2 (oxygen pressure = 1 atm). Thus, using Equation 18.37, it is necessary to solve for the time *t*. However, before this is possible, we must calculate the value of *B* from Equation 18.38a as follows:

$$B = 800 \exp\left(-\frac{1.24\ \text{eV}}{kT}\right) = (800) \exp\left[-\frac{1.24\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(900 + 273\ \text{K})}\right]$$

$$= 0.00378\ \mu m^2/h$$

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Now, solving for t from Equation 18.37 using the above value for B and that $x = 0.075$ μm, we have

$$t = \frac{x^2}{B} = \frac{(0.075\ \mu\text{m})^2}{0.00378\ \mu\text{m}^2/\text{h}}$$

$$= 1.49\ \text{h}$$

Repeating the computation for B at 750°C:

$$B = (800)\exp\left[-\frac{1.24\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(750 + 273\ \text{K})}\right]$$

$$= 6.25 \times 10^{-4}\ \mu\text{m}^2/\text{h}$$

And solving for the oxidation time as above

$$t = \frac{(0.075\ \mu\text{m})^2}{6.25 \times 10^{-4}\ \mu\text{m}^2/\text{h}} = 9.0\ \text{h}$$

(b) This part of the problem asks for us to compute the heating times to form an oxide layer 75 nm thick at the same two temperatures (900°C and 750°C) when the atmosphere is water vapor (1 atm pressure). At 900°C, the value of B is determined using Equation 18.38b, as follows:

$$B = 215\exp\left(-\frac{0.70\ \text{eV}}{kT}\right) = (215)\exp\left[-\frac{0.70\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(900 + 273\ \text{K})}\right]$$

$$= 0.212\ \mu\text{m}^2/\text{h}$$

And computation of the time t from the rearranged form of Equation 18.37, leads to

$$t = \frac{x^2}{B} = \frac{(0.075\ \mu\text{m})^2}{0.212\ \mu\text{m}^2/\text{h}}$$

$$= 0.0265\ \text{h} = 95.5\ \text{s}$$

And at 750°C, the value of B is

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$$B = (215)\exp\left[-\frac{0.70\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(750 + 273\ \text{K})}\right] = 0.0767\ \mu\text{m}^2/\text{h}$$

Whereas the time required to grow the 75 nm oxide layer is

$$t = \frac{x^2}{B} = \frac{(0.075\ \mu\text{m})^2}{0.0767\ \mu\text{m}^2/\text{h}}$$

$$= 0.073\ \text{h} = 264\ \text{s}$$

From the above computations, it is very apparent (1) that the 75 nm oxide layer forms more rapidly at 900°C (than at 750°C) in both O_2 and H_2O gaseous atmospheres, and (2) that the oxide layer formation is more rapid in water vapor than in oxygen.

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18.D8 *The base semiconducting material used in virtually all of our modern integrated circuits is silicon. However, silicon has some limitations and restrictions. Write an essay comparing the properties and applications (and/or potential applications) of silicon and gallium arsenide.*

Solution

We are asked to compare silicon and gallium arsenide semiconductors relative to properties and applications.

The following are the characteristics and applications for Si: (1) being an elemental semiconductor, it is cheaper to grow in single-crystalline form; (2) because of its electron band structure, it is best used in transistors; (3) electronic processes are relatively slow due to the low mobilities for electrons and holes (Table 18.3).

For GaAs: (1) it is much more expensive to produce inasmuch as it is a compound semiconductor; (2) because of its electron band structure it is best used in light-emitting diodes and semiconducting lasers; (3) its band gap may be altered by alloying; (4) electronic processes are more rapid than in Si due to the greater mobilities for electrons and holes; (5) absorption of electromagnetic radiation is greater in GaAs, and therefore, thinner layers are required for solar cells.

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CHAPTER 19

THERMAL PROPERTIES

PROBLEM SOLUTIONS

Heat Capacity

19.1 *Estimate the energy required to raise the temperature of 2 kg (4.42 lb_m) of the following materials from 20 to 100°C (68 to 212°F): aluminum, steel, soda–lime glass, and high-density polyethylene.*

Solution

The energy, E, required to raise the temperature of a given mass of material, m, is the product of the specific heat, the mass of material, and the temperature change, ΔT, as

$$E = c_p m \Delta T$$

The ΔT in this problem is equal to 100°C – 20°C = 80°C (= 80 K), while the mass is 2 kg, and the specific heats are presented in Table 19.1. Thus,

$$E(\text{aluminum}) = (900 \text{ J/kg - K})(2 \text{ kg})(80 \text{ K}) = 1.44 \times 10^5 \text{ J}$$

$$E(\text{steel}) = (486 \text{ J/kg - K})(2 \text{ kg})(80 \text{ K}) = 7.78 \times 10^4 \text{ J}$$

$$E(\text{glass}) = (840 \text{ J/kg - K})(2 \text{ kg})(80 \text{ K}) = 1.34 \times 10^5 \text{ J}$$

$$E(\text{HDPE}) = (1850 \text{ J/kg - K})(2 \text{ kg})(80 \text{ K}) = 2.96 \times 10^5 \text{ J}$$

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19.2 *To what temperature would 25 lb_m of a 1025 steel specimen at 25°C (77°F) be raised if 125 Btu of heat is supplied?*

Solution

We are asked to determine the temperature to which 25 lb_m of steel initially at 25°C would be raised if 125 Btu of heat is supplied. This is accomplished by utilization of a modified form of Equation 19.1 as

$$\Delta T = \frac{\Delta Q}{m c_p}$$

in which ΔQ is the amount of heat supplied, m is the mass of the specimen, and c_p is the specific heat. From Table 19.1, c_p = 486 J/kg-K for steel, which in Customary U.S. units is just

$$c_p = (486 \text{ J/kg - K})\left(\frac{2.39 \times 10^{-4} \text{ Btu/lb}_m \text{ - °F}}{1 \text{ J/kg - K}}\right) = 0.116 \text{ Btu/lb}_m \text{ - °F}$$

Thus

$$\Delta T = \frac{125 \text{ Btu}}{(25 \text{ lb}_m)(0.116 \text{ Btu/lb}_m \text{ - °F})} = 43.1°\text{F}$$

and

$$T_f = T_0 + \Delta T = 77°\text{F} + 43.1°\text{F} = 120.1°\text{F} \quad (49°\text{C})$$

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19.3 *(a) Determine the room temperature heat capacities at constant pressure for the following materials: aluminum, silver, tungsten, and 70Cu-30Zn brass. (b) How do these values compare with one another? How do you explain this?*

Solution

(a) This problem asks that we determine the room-temperature heat capacities at constant pressure, C_p, for aluminum, silver, tungsten, and 70Cu-30Zn brass. All we need do is multiply the c_p values in Table 19.1 by the atomic weights (values are found inside the front cover), taking into account the conversion from grams to kilograms (for the atomic weights). Thus, for Al

$$C_p = (900 \text{ J/kg - K})(1 \text{ kg}/1000 \text{ g})(26.98 \text{ g/mol}) = 24.3 \text{ J/mol - K}$$

For Ag

$$C_p = (235 \text{ J/kg - K})(1 \text{ kg}/1000 \text{ g})(107.87 \text{ g/mol}) = 25.4 \text{ J/mol - K}$$

For W

$$C_p = (138 \text{ J/kg - K})(1 \text{ kg}/1000 \text{ g})(183.84 \text{ g/mol}) = 25.4 \text{ J/mol - K}$$

For brass it is first necessary to compute the alloy atomic weight (A_{ave}) using Equation 4.11a as follows:

$$A_{\text{ave}} = \frac{100}{\frac{C_{\text{Cu}}}{A_{\text{Cu}}} + \frac{C_{\text{Zn}}}{A_{\text{Zn}}}}$$

$$= \frac{100}{\frac{70 \text{ wt\%}}{63.55 \text{ g/mol}} + \frac{30 \text{ wt\%}}{65.41 \text{ g/mol}}}$$

$$= 64.09 \text{ g/mol}$$

Thus

$$C_p = (375 \text{ J/kg - K})(1 \text{ kg}/1000 \text{ g})(64.09 \text{ g/mol}) = 24.0 \text{ J/mol - K}$$

(b) These values of C_p are very close to one another because room temperature is considerably above the Debye temperature for these metals; therefore, the values of C_p should be about equal to $3R$ [(3)(8.31 J/mol-K) = 24.9 J/mol-K], which is indeed the case for all four of these metals.

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19.4 *For aluminum, the heat capacity at constant volume C_v at 30 K is 0.81 J/mol-K, and the Debye temperature is 375 K. Estimate the specific heat (a) at 50 K and (b) at 425 K.*

Solution

(a) For aluminum, C_v at 50 K may be approximated by Equation 19.2, since this temperature is significantly below the Debye temperature (375 K). The value of C_v at 30 K is given, and thus, we may compute the constant A as

$$A = \frac{C_v}{T^3} = \frac{0.81 \text{ J/mol-K}}{(30 \text{ K})^3} = 3.00 \times 10^{-5} \text{ J/mol-K}^4$$

Therefore, at 50 K

$$C_v = AT^3 = (3.00 \times 10^{-5} \text{ J/mol-K}^4)(50 \text{ K})^3 = 3.75 \text{ J/mol-K}$$

and

$$c_v = (3.75 \text{ J/mol-K})(1 \text{ mol}/26.98 \text{ g})(1000 \text{ g/kg}) = 139 \text{ J/kg-K}$$

(b) Since 425 K is above the Debye temperature, a good approximation for C_v is

$$C_v = 3R$$

$$= (3)(8.31 \text{ J/mol-K}) = 24.9 \text{ J/mol-K}$$

And, converting this to specific heat

$$c_v = (24.9 \text{ J/mol-K})(1 \text{ mol}/26.98 \text{ g})(1000 \text{ g/kg}) = 923 \text{ J/kg-K}$$

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19.5 *The constant A in Equation 19.2 is $12\pi^4 R/5\,\theta_D^3$, where R is the gas constant and θ_D is the Debye temperature (K). Estimate θ_D for copper, given that the specific heat is 0.78 J/kg-K at 10 K.*

Solution

For copper, we want to compute the Debye temperature, θ_D, given the expression for A in Equation 19.2 and the heat capacity at 10 K. First of all, let us determine the magnitude of A, as

$$A = \frac{C_v}{T^3}$$

$$= \frac{(0.78\ \text{J/mol-K})(1\ \text{kg}/1000\ \text{g})(63.55\ \text{g/mol})}{(10\ \text{K})^3}$$

$$= 4.96 \times 10^{-5}\ \text{J/mol-K}^4$$

As stipulated in the problem statement

$$A = \frac{12\pi^4 R}{5\theta_D^3}$$

Or, solving for θ_D

$$\theta_D = \left(\frac{12\pi^4 R}{5A}\right)^{1/3}$$

$$= \left[\frac{(12)(\pi)^4(8.31\ \text{J/mol-K})}{(5)(4.96 \times 10^{-5}\ \text{J/mol-K}^4)}\right]^{1/3} = 340\ \text{K}$$

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19.6 *(a) Briefly explain why C_v rises with increasing temperature at temperatures near 0 K. (b) Briefly explain why C_v becomes virtually independent of temperature at temperatures far removed from 0 K.*

Solution

(a) The reason that C_v rises with increasing temperature at temperatures near 0 K is because, in this temperature range, the allowed vibrational energy levels of the lattice waves are far apart relative to the available thermal energy, and only a portion of the lattice waves may be excited. As temperature increases, more of the lattice waves may be excited by the available thermal energy, and, hence, the ability of the solid to absorb energy (i.e., the magnitude of the heat capacity) increases.

(b) At temperatures far removed from 0 K, C_v becomes independent of temperature because all of the lattice waves have been excited and the energy required to produce an incremental temperature change is nearly constant.

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Thermal Expansion

19.7 *An aluminum wire 10 m (32.8 ft) long is cooled from 38 to -1°C (100 to 30°F). How much change in length will it experience?*

Solution

In order to determine the change in length of the aluminum wire, we must employ a rearranged form of Equation 19.3b and using the value of α_l taken from Table 19.1 [23.6×10^{-6} $(°C)^{-1}$] as

$$\Delta l = l_0 \alpha_l \Delta T = l_0 \alpha_l (T_f - T_0)$$

$$= (10 \text{ m}) \left[23.6 \times 10^{-6} (°C)^{-1}\right](-1°C - 38°C)$$

$$= -9.2 \times 10^{-3} \text{ m} = -9.2 \text{ mm} \quad (-0.36 \text{ in.})$$

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19.8 *A 0.1 m (3.9 in.) rod of a metal elongates 0.2 mm (0.0079 in.) on heating from 20 to 100°C (68 to 212°F). Determine the value of the linear coefficient of thermal expansion for this material.*

Solution

The linear coefficient of thermal expansion for this material may be determined using a rearranged form of Equation 19.3b as

$$\alpha_l = \frac{\Delta l}{l_0 \Delta T} = \frac{\Delta l}{l_0 (T_f - T_0)} = \frac{0.2 \times 10^{-3}\ \text{m}}{(0.1\ \text{m})(100°\text{C} - 20°\text{C})}$$

$$= 25.0 \times 10^{-6}\ (°\text{C})^{-1}$$

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19.9 *Briefly explain thermal expansion using the potential energy-versus-interatomic spacing curve.*

The phenomenon of thermal expansion using the potential energy-versus-interatomic spacing curve is explained in Section 19.3.

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19.10 *Compute the density for nickel at 500°C, given that its room-temperature density is 8.902 g/cm^3. Assume that the volume coefficient of thermal expansion, α_v, is equal to $3\alpha_l$.*

Solution

In this problem we are asked to determine the density of nickel at 500°C. Let us use as the basis for this determination 1 cm^3 of material at 20°C, which has a mass of 8.902 g; it is assumed that this mass will remain constant upon heating to 500°C. Let us compute the volume expansion of this cubic centimeter of nickel as it is heated to 500°C. A volume expansion expression is given in Equation 19.4—viz.,

$$\frac{\Delta V}{V_0} = \alpha_v \Delta T$$

or

$$\Delta V = V_0 \alpha_v \Delta T$$

Also, $\alpha_v = 3\alpha_l$, as stipulated in the problem. The value of α_l given in Table 19.1 for nickel is 13.3×10^{-6} (°C)$^{-1}$. Therefore, the volume, V, of this specimen of Ni at 500°C is just

$$V = V_0 + \Delta V = V_0(1 + \alpha_v \Delta T) = V_0(1 + 3\alpha_l \Delta T)$$

$$= (1\ \text{cm}^3)\left\{1 + (3)\left[13.3 \times 10^{-6}\ (°\text{C})^{-1}\right](500°\text{C} - 20°\text{C})\right\}$$

$$= 1.01915\ \text{cm}^3$$

Thus, the density is just the 8.902 g divided by this new volume—i.e.,

$$\rho = \frac{8.902\ \text{g}}{1.01915\ \text{cm}^3} = 8.735\ \text{g/cm}^3$$

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19.11 *When a metal is heated its density decreases. There are two sources that give rise to this diminishment of ρ: (1) the thermal expansion of the solid, and (2) the formation of vacancies (Section 4.2). Consider a specimen of copper at room temperature (20°C) that has a density of 8.940 g/cm^3. (a) Determine its density upon heating to 1000°C when only thermal expansion is considered. (b) Repeat the calculation when the introduction of vacancies is taken into account. Assume that the energy of vacancy formation is 0.90 eV/atom, and that the volume coefficient of thermal expansion, α_v is equal to $3\alpha_l$.*

Solution

(a) In this portion of the problem we are asked to determine the density of copper at 1000°C on the basis of thermal expansion considerations. The basis for this determination will be 1 cm^3 of material at 20°C; this volume of copper has a mass of 8.940 g, which mass is assumed to remain constant upon heating to the 1000°C. Let us first compute the volume expansion of this cubic centimeter of copper as it is heated to 1000°C. According to Equation 19.4 volume expansion is equal to

$$\frac{\Delta V}{V_0} = \alpha_v \Delta T$$

where α_v, the volume coefficient of thermal expansion, as stipulated in the problem statement, is equal to $3\alpha_l$. The value of α_l given in Table 19.1 for copper is 17.0×10^{-6} (°C)$^{-1}$. Therefore, the volume of this specimen of Cu at 1000°C (V) is equal to

$$V = V_0 + \Delta V = V_0 + V_0 \alpha_v \Delta T = V_0 (1 + \alpha_v \Delta T)$$

$$= V_0 (1 + 3\alpha_l \Delta T) = V_0 \left[1 + 3\alpha_l (T_f - T_0)\right]$$

$$= (1 \text{ cm}^3) \left\{1 + (3)\left[17.0 \times 10^{-6} (°\text{C})^{-1}\right](1000°\text{C} - 20°\text{C})\right\}$$

$$= 1.04998 \text{ cm}^3$$

Thus, the density is just the 8.940 g divided by this new volume—i.e.,

$$\rho = \frac{8.940 \text{ g}}{1.04998 \text{ cm}^3} = 8.514 \text{ g/cm}^3$$

(b) Now we are asked to compute the density at 1000°C taking into consideration the creation of vacancies which will further lower the density. To begin, this determination requires that we calculate the number

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of vacancies using Equation 4.1. But it first becomes necessary to compute the number of Cu atoms per cubic centimeter (N_{Cu}) at 1000°C using Equation 4.2. Thus,

$$N_{Cu} = \frac{N_A \rho_{Cu}}{A_{Cu}}$$

$$= \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(8.514\ \text{g/cm}^3)}{63.55\ \text{g/mol}}$$

$$= 8.07 \times 10^{22}\ \text{atoms/cm}^3$$

Now, from Equation 4.1, the total number of vacancies, N_v, is computed as

$$N_v = N_{Cu} \exp\left(-\frac{Q_v}{kT}\right)$$

$$= (8.07 \times 10^{22}\ \text{atoms/cm}^3) \exp\left[-\frac{0.90\ \text{eV/atom}}{(8.62 \times 10^{-5}\ \text{eV/K})(1000 + 273\ \text{K})}\right]$$

$$= 2.212 \times 10^{19}\ \text{vacancies/cm}^3$$

We now want to determine the number of vacancies per unit cell, which is possible if the unit cell volume is multiplied by N_v. The unit cell volume (V_C) may be calculated using Equation 3.5 taking $n = 4$ inasmuch as Cu has the FCC crystal structure. Thus, from a rearranged form of Equation 3.5

$$V_C = \frac{nA_{Cu}}{\rho_{Cu} N_A}$$

$$= \frac{(4\ \text{atoms/unit cell})(63.55\ \text{g/mol})}{(8.514\ \text{g/cm}^3)(6.022 \times 10^{23}\ \text{atoms/mol})}$$

$$= 4.958 \times 10^{-23}\ \text{cm}^3\text{/unit cell}$$

Now, the number of vacancies per unit cell, n_v, is just

$$n_v = N_v V_C$$

$$= (2.212 \times 10^{19}\ \text{vacancies/cm}^3)(4.958 \times 10^{-23}\ \text{cm}^3\text{/unit cell})$$

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$$= 0.001097 \text{ vacancies/unit cell}$$

What this means is that instead of there being 4.0000 atoms per unit cell, there are only 4.0000 – 0.001097 = 3.998903 atoms per unit cell. And, finally, the density may be computed using Equation 3.5 taking n = 3.998903; thus

$$\rho_{Cu} = \frac{nA_{Cu}}{V_C N_A}$$

$$= \frac{(3.998903 \text{ atoms/unit cell})(63.55 \text{ g/mol})}{(4.958 \times 10^{-23} \text{ cm}^3\text{/unit cell})(6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 8.512 \text{ g/cm}^3$$

Thus, the influence of the vacancies is almost insignificant--their presence reduces the density by only 0.002 g/cm^3 (from 8.514 g/cm^3 to 8.512 g/cm^3).

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19.12 *The difference between the specific heats at constant pressure and volume is described by the expression*

$$c_p - c_v = \frac{\alpha_v^2 v_0 T}{\beta} \qquad (19.10)$$

where α_v is the volume coefficient of thermal expansion, v_0 is the specific volume (i.e., volume per unit mass, or the reciprocal of density), β is the compressibility, and T is the absolute temperature. Compute the values of c_v at room temperature (293 K) for copper and nickel using the data in Table 19.1, assuming that $\alpha_v = 3\alpha_l$ and given that the values of β for Cu and Ni are 8.35×10^{-12} and 5.51×10^{-12} $(Pa)^{-1}$, respectively.

Solution

This problem asks that we calculate the values of c_v for copper and nickel at room temperature using Equation 19.10, the data in Table 19.1, given that $\alpha_v = 3\alpha_l$, and also values of the compressibility. From Equation 19.10

$$c_v = c_p - \frac{\alpha_v^2 v_0 T}{\beta}$$

And, from Table 19.1 and the problem statement

c_p(Cu) = 386 J/kg-K
c_p(Ni) = 443 J/kg-K
α_v(Cu) = (3)[17.0×10^{-6} $(°C)^{-1}$] = 5.10×10^{-5} $(°C)^{-1}$
α_v(Ni) = (3)[(13.3×10^{-6} $(°C)^{-1}$] = 3.99×10^{-5} $(°C)^{-1}$
β(Cu) = 8.35×10^{-12} $(Pa)^{-1}$
β(Ni) = 5.51×10^{-12} $(Pa)^{-1}$

The specific volume is just the reciprocal of the density; thus, in units of m^3/kg

$$v_0(\text{Cu}) = \frac{1}{\rho} = \left(\frac{1}{8.94\ \text{g/cm}^3}\right)\left(\frac{1000\ \text{g}}{\text{kg}}\right)\left(\frac{1\ \text{m}}{100\ \text{cm}}\right)^3 = 1.119 \times 10^{-4}\ \text{m}^3/\text{kg}$$

$$v_0(\text{Ni}) = \left(\frac{1}{8.90\ \text{g/cm}^3}\right)\left(\frac{1000\ \text{g}}{\text{kg}}\right)\left(\frac{1\ \text{m}}{100\ \text{cm}}\right)^3 = 1.124 \times 10^{-4}\ \text{m}^3/\text{kg}$$

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Therefore, for copper

$$c_v(\text{Cu}) = c_p(\text{Cu}) - \frac{\alpha_v^2(\text{Cu})\, v_0(\text{Cu})T}{\beta(\text{Cu})}$$

$$= 386\ \text{J/kg - K} - \frac{\left[5.10 \times 10^{-5}\ (^{\circ}\text{C})^{-1}\right]^2 (1.119 \times 10^{-4}\ \text{m}^3/\text{kg})(293\ \text{K})}{8.35 \times 10^{-12}\ (\text{N/m}^2)^{-1}}$$

$$= 376\ \text{J/kg-K}$$

And, also for nickel

$$c_v(\text{Ni}) = 443\ \text{J/kg - K} - \frac{\left[3.99 \times 10^{-5}\ (^{\circ}\text{C})^{-1}\right]^2 (1.124 \times 10^{-4}\ \text{m}^3/\text{kg})(293\ \text{K})}{5.51 \times 10^{-12}\ (\text{N/m}^2)^{-1}}$$

$$= 433\ \text{J/kg-K}$$

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19.13 *To what temperature must a cylindrical rod of tungsten 10.000 mm in diameter and a plate of 316 stainless steel having a circular hole 9.988 mm in diameter have to be heated for the rod to just fit into the hole? Assume that the initial temperature is 25°C.*

Solution

This problem asks for us to determine the temperature to which a cylindrical rod of tungsten 10.000 mm in diameter must be heated in order for it of just fit into a 9.988 mm diameter circular hole in a plate of 316 stainless steel, assuming that the initial temperature is 25°C. This requires the use of Equation 19.3a, which is applied to the diameters of both the rod and hole. That is

$$\frac{d_f - d_0}{d_0} = \alpha_l (T_f - T_0)$$

Solving this expression for d_f yields

$$d_f = d_0 \left[1 + \alpha_l (T_f - T_0) \right]$$

Now all we need do is to establish expressions for d_f(316 stainless) and d_f(W), set them equal to one another, and solve for T_f. According to Table 19.1, α_l(316 stainless) = 16.0×10^{-6} $(°C)^{-1}$ and α_l(W) = 4.5×10^{-6} $(°C)^{-1}$. Thus

$$d_f(\text{316 stainless}) = d_f(\text{W})$$

$$(9.988\ \text{mm}) \left[1 + \left\{ 16.0 \times 10^{-6} (°C)^{-1} \right\} (T_f - 25°C) \right]$$

$$= (10.000\ \text{mm}) \left[1 + \left\{ 4.5 \times 10^{-6} (°C)^{-1} \right\} (T_f - 25°C) \right]$$

Now solving for T_f gives T_f = 129.5°C

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Thermal Conductivity

19.14 *(a) Calculate the heat flux through a sheet of steel 10 mm (0.39 in.) thick if the temperatures at the two faces are 300 and 100°C (572 and 212°F); assume steady-state heat flow. (b) What is the heat loss per hour if the area of the sheet is 0.25 m^2 (2.7 ft^2)? (c) What will be the heat loss per hour if soda–lime glass instead of steel is used? (d) Calculate the heat loss per hour if steel is used and the thickness is increased to 20 mm (0.79 in.).*

Solution

(a) The steady-state heat flux through the plate may be computed using Equation 19.5; the thermal conductivity for steel, found in Table 19.1, is 51.9 W/m-K. Therefore,

$$q = -k\frac{\Delta T}{\Delta x}$$

$$= -(51.9\ \text{W/m-K})\left[\frac{(100 + 273\ \text{K}) - (300 + 273\ \text{K})}{10 \times 10^{-3}\ \text{m}}\right]$$

$$= 1.04 \times 10^6\ \text{W/m}^2$$

(b) Let dQ/dt represent the total heat loss such that

$$\frac{dQ}{dt} = qAt$$

where A and t are the cross-sectional area and time, respectively. Thus,

$$\frac{dQ}{dt} = (1.04 \times 10^6\ \text{J/s-m}^2)(0.25\ \text{m}^2)(60\ \text{s/min})(60\ \text{min/h})$$

$$= 9.3 \times 10^8\ \text{J/h} \quad (8.9 \times 10^5\ \text{Btu/h})$$

(c) If soda-lime glass is used (k = 1.7 W/m-K, Table 19.1),

$$\frac{dQ}{dt} = -kAt\frac{\Delta T}{\Delta x}$$

$$= -(1.7\ \text{J/s-m-K})(0.25\ \text{m}^2)(3600\ \text{s/h})\left(\frac{-200\ \text{K}}{10 \times 10^{-3}\ \text{m}}\right)$$

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$$= 3.06 \times 10^7 \text{ J/h} \quad (2.9 \times 10^4 \text{ Btu/h})$$

(d) If the thickness of the steel is increased to 20 mm, then

$$\frac{dQ}{dt} = -kAt\frac{\Delta T}{\Delta x} = -(51.9 \text{ W/m-K})(0.25 \text{ m}^2)(3600 \text{ s/h})\left(\frac{-200 \text{ K}}{20 \times 10^{-3} \text{ m}}\right)$$

$$= 4.7 \times 10^8 \text{ J/h} \quad (4.5 \times 10^5 \text{ Btu/h})$$

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19.15 *(a) Would you expect Equation 19.7 to be valid for ceramic and polymeric materials? Why or why not? (b) Estimate the value for the Wiedemann–Franz constant L [in Ω-W/(K)^2] at room temperature (293 K) for the following nonmetals: silicon (intrinsic), glass-ceramic (Pyroceram), fused silica, polycarbonate, and polytetrafluoroethylene. Consult Tables B.7 and B.9 in Appendix B.*

Solution

(a) Equation 19.7 is not valid for ceramic and polymeric materials since, in the development of this expression, it is assumed that free electrons are responsible for both electrical and thermal conduction. Such is the case for most metals. For ceramics and polymers, free electrons are the primary contributors to the electrical conductivity. However, free electrons do not contribute significantly to the thermal conductivity. For ceramics, thermal conduction is primarily by means of phonons; for polymers, the energy transfer is made by chain vibrations, translations, and rotations.

(b) Estimated room-temperature values of L, in Ω-W/(K)^2, for the several materials are determined below. Electrical conductivity values were determined by taking reciprocals of the electrical resistivities given in Table B.9, Appendix B; thermal conductivities are taken from Table B.7 in the same appendix. (*Note:* when a range of values is given in these tables, an average value is used in the computation.)

For intrinsic silicon

$$L = \frac{k}{\sigma T} = \frac{141 \text{ W/m-K}}{\left[\frac{1}{2500 \text{ } (\Omega - \text{m})}\right](293 \text{ K})} = 1203 \text{ } \Omega\text{-W/K}^2$$

For Pyroceram glass-ceramic

$$L = \frac{3.3 \text{ W/m-K}}{\left[\frac{1}{2 \times 10^{-14} \text{ } (\Omega - \text{m})}\right](293 \text{ K})} = 2.3 \times 10^{12} \text{ } \Omega\text{-W/K}^2$$

For fused silica

$$L = \frac{1.4 \text{ W/m-K}}{\left[\frac{1}{10^{18} \text{ } (\Omega - \text{m})}\right](293 \text{ K})} = 4.8 \times 10^{15} \text{ } \Omega\text{-W/K}^2$$

For polycarbonate

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$$L = \frac{0.20 \ \text{W/m-K}}{\left[\frac{1}{2 \times 10^{14} \ (\Omega - \text{m})}\right](293 \ \text{K})} = 1.4 \times 10^{11} \ \ \Omega\text{-W/K}^2$$

For polytetrafluoroethylene

$$L = \frac{0.25 \ \text{W/m-K}}{\left[\frac{1}{10^{17} \ (\Omega - \text{m})}\right](293 \ \text{K})} = 8.5 \times 10^{13} \ \ \Omega\text{-W/K}^2$$

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19.16 *Briefly explain why the thermal conductivities are higher for crystalline than noncrystalline ceramics.*

Solution

Thermal conductivities are higher for crystalline than for noncrystalline ceramics because, for noncrystalline, phonon scattering, and thus the resistance to heat transport, is much more effective due to the highly disordered and irregular atomic structure.

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19.17 *Briefly explain why metals are typically better thermal conductors than ceramic materials.*

Solution

Metals are typically better thermal conductors than are ceramic materials because, for metals, most of the heat is transported by free electrons (of which there are relatively large numbers). In ceramic materials, the primary mode of thermal conduction is via phonons, and phonons are more easily scattered than are free electrons.

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19.18 *(a) Briefly explain why porosity decreases the thermal conductivity of ceramic and polymeric materials, rendering them more thermally insulative. (b) Briefly explain how the degree of crystallinity affects the thermal conductivity of polymeric materials and why.*

Solution

(a) Porosity decreases the thermal conductivity of ceramic and polymeric materials because the thermal conductivity of a gas phase that occupies pore space is extremely small relative to that of the solid material. Furthermore, contributions from gaseous convection are generally insignificant.

(b) Increasing the degree of crystallinity of a semicrystalline polymer enhances its thermal conductivity; the vibrations, rotations, etc. of the molecular chains are more effective modes of thermal transport when a crystalline structure prevails.

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19.19 *For some ceramic materials, why does the thermal conductivity first decrease and then increase with rising temperature?*

Solution

For some ceramic materials, the thermal conductivity first decreases with rising temperature because the scattering of lattice vibrations increases with temperature. At higher temperatures, the thermal conductivity will increase for some ceramics that are porous because radiant heat transfer across pores may become important, which process increases with rising temperature.

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19.20 *For each of the following pairs of materials, decide which has the larger thermal conductivity. Justify your choices.*

(a) Pure copper; aluminum bronze (95 wt% Cu-5 wt% Al).

(b) Fused silica; quartz.

(c) Linear polyethylene; branched polyethylene.

(d) Random poly(styrene-butadiene) copolymer; alternating poly(styrene-butadiene) copolymer.

Solution

This question asks for us to decide, for each of several pairs of materials, which has the larger thermal conductivity and why.

(a) Pure copper will have a larger conductivity than aluminum bronze because the impurity atoms in the latter will lead to a greater degree of free electron scattering.

(b) Quartz will have a larger conductivity than fused silica because fused silica is noncrystalline (whereas quartz is crystalline) and lattice vibrations are more effectively scattered in noncrystalline materials.

(c) The linear polyethylene will have the larger conductivity than the branched polyethylene because the former will have the higher degree of crystallinity. Linear polymers have higher degrees of crystallinity than branched polymers. Since heat transfer is accomplished by molecular chain vibrations, and the coordination of these vibrations increases with percent crystallinity, the higher the crystallinity, the greater the thermal conductivity.

(d) The alternating poly(styrene-butadiene) copolymer will have a higher crystallinity than the random copolymer; alternating copolymers crystallize more easily than random ones. The influence of crystallinity on conductivity is explained in part (c).

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19.21 *We might think of a porous material as being a composite wherein one of the phases is a pore phase. Estimate upper and lower limits for the room-temperature thermal conductivity of a magnesium oxide material having a volume fraction of 0.30 of pores that are filled with still air.*

Solution

This problem asks that we treat a porous material as a composite wherein one of the phases is a pore phase, and that we estimate upper and lower limits for the room-temperature thermal conductivity of a magnesium oxide material having a 0.30 volume fraction of pores. The upper limit of k (k_{upper}) may be determined using Equation 16.1 with thermal conductivity substituted for the elastic modulus, E. From Table 19.1, the value of k for MgO is 37.7 W/m-K, while for still air in the pore phase, k = 0.02 W/m-K (Section 19.4). Thus

$$k_{upper} = V_p k_{air} + V_{MgO} k_{MgO}$$

$$= (0.30)(0.02 \text{ W/m-K}) + (0.70)(37.7 \text{ W/m-K}) = 26.4 \text{ W/m-K}$$

For the lower limit we employ a modification of Equation 16.2 as

$$k_{lower} = \frac{k_{air} k_{MgO}}{V_p k_{MgO} + V_{MgO} k_{air}}$$

$$= \frac{(0.02 \text{ W/m-K})(37.7 \text{ W/m-K})}{(0.30)(37.7 \text{ W/m-K}) + (0.70)(0.02 \text{ W/m-K})} = 0.067 \text{ W/m-K}$$

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19.22 *Nonsteady-state heat flow may be described by the following partial differential equation:*

$$\frac{\partial T}{\partial t} = D_T \frac{\partial^2 T}{\partial x^2}$$

where D_T is the thermal diffusivity; this expression is the thermal equivalent of Fick's second law of diffusion (Equation 5.4b). The thermal diffusivity is defined according to

$$D_T = \frac{k}{\rho c_p}$$

In this expression, k, ρ, and c_p represent the thermal conductivity, the mass density, and the specific heat at constant pressure, respectively.

(a) What are the SI units for D_T?

(b) Determine values of D_T for aluminum, steel, aluminum oxide, soda–lime glass, polystyrene, and nylon 6,6 using the data in Table 19.1. Density values are included in Table B.1, Appendix B.

Solution

(a) The units of D_T are

$$D_T = \frac{k\,(\text{J/s - m - K})}{\rho(\text{kg/m}^3)\,c_p(\text{J/kg - K})} = \text{m}^2/\text{s}$$

(b) The values of D_T for the several materials are given below. (Note: values for k and c_p are taken from Table 19.1; density values are from Table B.1, Appendix B, and converted to units of kilograms per meter cubed):

For aluminum

$$D_T = \frac{k}{\rho\, c_p} = \frac{247\ \text{W/m - K}}{(2.71 \times 10^3\ \text{kg/m}^3)(900\ \text{J/kg - K})} = 1.0 \times 10^{-4}\ \text{m}^2/\text{s}$$

For steel

$$D_T = \frac{51.9\ \text{W/m - K}}{(7.9 \times 10^3\ \text{kg/m}^3)(486\ \text{J/kg - K})} = 1.4 \times 10^{-5}\ \text{m}^2/\text{s}$$

For aluminum oxide

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$$D_T = \frac{39 \text{ W/m - K}}{(4 \times 10^3 \text{ kg/m}^3)(775 \text{ J/kg - K})} = 1.26 \times 10^{-5} \text{ m}^2/\text{s}$$

For soda-lime glass

$$D_T = \frac{1.7 \text{ W/m - K}}{(2.5 \times 10^3 \text{ kg/m}^3)(840 \text{ J/kg - K})} = 8.1 \times 10^{-7} \text{ m}^2/\text{s}$$

For polystyrene

$$D_T = \frac{0.13 \text{ W/m - K}}{(1.05 \times 10^3 \text{ kg/m}^3)(1170 \text{ J/kg - K})} = 1.06 \times 10^{-7} \text{ m}^2/\text{s}$$

For nylon 6,6

$$D_T = \frac{0.24 \text{ W/m - K}}{(1.14 \times 10^3 \text{ kg/m}^3)(1670 \text{ J/kg - K})} = 1.3 \times 10^{-7} \text{ m}^2/\text{s}$$

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Thermal Stresses

19.23 *Beginning with Equation 19.3, show that Equation 19.8 is valid.*

Solution

We want to show that Equation 19.8 is valid beginning with Equation 19.3. Upon examination of Equation 19.3b,

$$\frac{\Delta l}{l_0} = \alpha_l \Delta T$$

it may be noted that the term on the left-hand side is the same expression as that for the definition of engineering strain (Equation 6.2); that is

$$\varepsilon = \frac{\Delta l}{l_0}$$

Furthermore, elastic stress and strain are related through Hooke's law, Equation 6.5:

$$\sigma = E\varepsilon$$

Making appropriate substitutions and algebraic manipulations gives

$$\frac{\Delta l}{l_0} = \varepsilon = \frac{\sigma}{E} = \alpha_l \Delta T$$

Or, solving for σ

$$\sigma = E\alpha_l \Delta T$$

which is the form of Equation 19.8.

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19.24 *(a) Briefly explain why thermal stresses may be introduced into a structure by rapid heating or cooling. (b) For cooling, what is the nature of the surface stresses? (c) For heating, what is the nature of the surface stresses?*

Solution

(a) Thermal stresses may be introduced into a structure by rapid heating or cooling because temperature gradients will be established across the cross section due to more rapid temperature changes at the surface than within the interior; thus, the surface will expand or contract at a different rate than the interior and since this surface expansion or contraction will be restrained by the interior, stresses will be introduced.

(b) For cooling, the surface stresses will be tensile in nature since the interior contracts to a lesser degree than the cooler surface.

(c) For heating, the surface stresses will be compressive in nature since the interior expands to a lesser degree than the hotter surface.

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19.25 *(a) If a rod of 1025 steel 0.5 m (19.7 in.) long is heated from 20 to 80°C (68 to 176°F) while its ends are maintained rigid, determine the type and magnitude of stress that develops. Assume that at 20°C the rod is stress free. (b) What will be the stress magnitude if a rod 1 m (39.4 in.) long is used? (c) If the rod in part (a) is cooled from 20 to -10°C (68 to 14°F), what type and magnitude of stress will result?*

Solution

(a) We are asked to compute the magnitude of the stress within a 1025 steel rod that is heated while its ends are maintained rigid. To do this we employ Equation 19.8, using a value of 207 GPa for the modulus of elasticity of steel (Table 6.1), and a value of $12.0 \times 10^{-6}\ (°C)^{-1}$ for α_l (Table 19.1). Therefore

$$\sigma = E\alpha_l(T_0 - T_f)$$

$$= (207 \times 10^3\ \text{MPa})\left[12.0 \times 10^{-6}(°C)^{-1}\right](20°C - 80°C)$$

$$= -150\ \text{MPa} \quad (-21{,}800\ \text{psi})$$

The stress will be compressive since its sign is negative.

(b) The stress will be the same [–150 MPa (–21,800 psi)], since stress is independent of bar length.

(c) Upon cooling the indicated amount, the stress becomes

$$\sigma = E\alpha_l(T_0 - T_f)$$

$$= (207 \times 10^3\ \text{MPa})\left[12.0 \times 10^{-6}(°C)^{-1}\right][(20°C - (-10°C)]$$

$$= +74.5\ \text{MPa} \quad (+10{,}900\ \text{psi})$$

This stress will be tensile since its sign is positive.

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19.26 *A copper wire is stretched with a stress of 70 MPa (10,000 psi) at 20°C (68°F). If the length is held constant, to what temperature must the wire be heated to reduce the stress to 35 MPa (5000 psi)?*

Solution

We want to heat the copper wire in order to reduce the stress level from 70 MPa to 35 MPa; in doing so, we reduce the stress in the wire by 70 MPa – 35 MPa = 35 MPa, which stress will be a compressive one (i.e., $\sigma = -35$ MPa). Solving for T_f from Equation 19.8 [and using values for E and α_l of 110 GPa (Table 6.1) and 17.0×10^{-6} $(°C)^{-1}$ (Table 19.1), respectively] yields

$$T_f = T_0 - \frac{\sigma}{E\alpha_l}$$

$$= 20°C - \frac{-35 \text{ MPa}}{\left(110 \times 10^3 \text{ MPa}\right)\left[17.0 \times 10^{-6} \ (°C)^{-1}\right]}$$

$$= 20°C + 19°C = 39°C \ \ (101°F)$$

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19.27 *If a cylindrical rod of nickel 100.00 mm long and 8.000 mm in diameter is heated from 20°C to 200°C while its ends are maintained rigid, determine its change in diameter. You may want to consult Table 6.1.*

Solution

This problem asks for us to determine the change in diameter of a cylindrical nickel rod 100.00 mm long and 8.000 mm in diameter when it is heated from 20°C to 200°C while its ends are maintained rigid. There will be two contributions to the diameter increase of the rod; the first is due to thermal expansion (which will be denoted as Δd_1), while the second is from Poisson's lateral expansion as a result of elastic deformation from stresses that are established from the inability of the rod to elongate as it is heated (denoted as Δd_2). The magnitude of Δd_1 may be computed using a modified form of Equation 19.3 as

$$\Delta d_1 = d_0 \alpha_l (T_f - T_0)$$

From Table 19.1 the value of α_l for nickel is 13.3×10^{-6} $(°C)^{-1}$. Thus,

$$\Delta d_1 = (8.000 \text{ mm}) \left[13.3 \times 10^{-6} \ (°C)^{-1}\right](200°C - 20°C)$$

$$= 0.0192 \text{ mm}$$

Now, Δd_2 is related to the transverse strain (ε_x) according to a modified form of Equation 6.2 as

$$\frac{\Delta d_2}{d_0} = \varepsilon_x$$

Also, transverse strain and longitudinal strain (ε_z) are related according to Equation 6.8:

$$\varepsilon_x = - \nu \varepsilon_z$$

where ν is Poisson's ratio. Substitution of this expression for ε_x into the first equation above leads to

$$\frac{\Delta d_2}{d_0} = - \nu \varepsilon_z$$

Furthermore, the longitudinal strain is related to the modulus of elasticity through Equation 6.5—i.e.,

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$$\varepsilon_z = \frac{\sigma}{E}$$

And, therefore,

$$\frac{\Delta d_2}{d_0} = -\nu\frac{\sigma}{E}$$

Now, from Equation 19.8 stress is equal to

$$\sigma = E\alpha_l(T_0 - T_f)$$

which, when substituted into the preceding equation leads to

$$\frac{\Delta d_2}{d_0} = -\frac{\nu E\alpha_l(T_0 - T_f)}{E} = -\nu\alpha_l(T_0 - T_f)$$

Solving for Δd_2 and realizing that, for nickel, $\nu = 0.31$ (Table 6.1) yields

$$\Delta d_2 = -d_0\nu\alpha_l(T_0 - T_f)$$

$$= -(8.000\text{ mm})(0.31)\left[13.3 \times 10^{-6}\ (^\circ\text{C})^{-1}\right](20^\circ\text{C} - 200^\circ\text{C})$$

$$= 0.0059\text{ mm}$$

Finally, the total Δd is just $\Delta d_1 + \Delta d_2 = 0.0192\text{ mm} + 0.0059\text{ mm} = 0.0251\text{ mm}$.

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19.28 *The two ends of a cylindrical rod of 1025 steel 75.00 mm long and 10.000 mm in diameter are maintained rigid. If the rod is initially at 25°C, to what temperature must it be cooled to have a 0.008-mm reduction in diameter?*

Solution

This problem asks for us to determine to what temperature a cylindrical rod of 1025 steel 75.00 mm long and 10.000 mm in diameter must be cooled from 25°C in order to have a 0.008 mm reduction in diameter if the rod ends are maintained rigid. There will be two contributions to the diameter decrease of the rod; the first is due to thermal contraction (which will be denoted as Δd_1), while the second is from Poisson's lateral contraction as a result of elastic deformation from stresses that are established from the inability of the rod to contract as it is cooled (denoted as Δd_2). The magnitude of Δd_1 may be computed using a modified form of Equation 19.3b as

$$\Delta d_1 = d_0 \alpha_l (T_f - T_0)$$

Now, Δd_2 is related to the transverse strain (ε_x) according to a modified form of Equation 6.2 as

$$\frac{\Delta d_2}{d_0} = \varepsilon_x$$

Also, transverse strain and longitudinal strain (ε_z) are related according to Equation 6.8:

$$\varepsilon_x = -\nu\varepsilon_z$$

where ν is Poisson's ratio. Substitution of this expression for ε_x into the first equation above leads to

$$\frac{\Delta d_2}{d_0} = -\nu\varepsilon_z$$

Furthermore, the longitudinal strain is related to the modulus of elasticity through Equation 6.5—i.e.,

$$\varepsilon_z = \frac{\sigma}{E}$$

And, therefore,

$$\frac{\Delta d_2}{d_0} = -\nu\frac{\sigma}{E}$$

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Now, from Equation 19.8 stress is equal to

$$\sigma = E\alpha_l(T_0 - T_f)$$

which, when substituted into the preceding equation leads to

$$\frac{\Delta d_2}{d_0} = -\frac{\nu E\alpha_l(T_0 - T_f)}{E} = -\nu\alpha_l(T_0 - T_f)$$

And, solving for Δd_2 from this expression

$$\Delta d_2 = -d_0\nu\alpha_l(T_0 - T_f)$$

The total Δd is just $\Delta d = \Delta d_1 + \Delta d_2$, and

$$\Delta d = d_0\alpha_l(T_f - T_0) + d_0\nu\alpha_l(T_f - T_0) = d_0\alpha_l(T_f - T_0)(1 + \nu)$$

The values of ν and α_l for 1025 steel are 0.30 and 12.0×10^{-6} $(°C)^{-1}$, respectively (Tables 6.1 and 19.1). Incorporating, into the above equation, these values, as well as those for Δd, d_0, and T_0 cited in the problem statement gives

$$-(0.008\text{ mm}) = (10.000\text{ mm})\left[12.0 \times 10^{-6}\ (°C)^{-1}\right](T_f - 25°C)(1 + 0.30)$$

And, finally, solving the above expression for T_f yields $T_f = -26.3°C$.

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19.29 *What measures may be taken to reduce the likelihood of thermal shock of a ceramic piece?*

Solution

According to Equation 19.9, the thermal shock resistance of a ceramic piece may be enhanced by increasing the fracture strength and thermal conductivity, and by decreasing the elastic modulus and linear coefficient of thermal expansion. Of these parameters, σ_f and α_l are most amenable to alteration, usually be changing the composition and/or the microstructure.

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DESIGN PROBLEMS

Thermal Expansion

19.D1 *Railroad tracks made of 1025 steel are to be laid during the time of year when the temperature averages 10°C (50°F). If a joint space of 4.6 mm (0.180 in.) is allowed between the standard 11.9-m (39-ft) long rails, what is the hottest possible temperature that can be tolerated without the introduction of thermal stresses?*

Solution

For these railroad tracks, each end is allowed to expand one-half of the joint space distance, or the track may expand a total of this distance (4.6 mm). Equation 19.3a is used to solve for T_f, where the value α_l for the 1025 steel [12.0×10^{-6} $(°C)^{-1}$] is found in Table 19.1. Thus, solving for T_f from Equation 19.3a leads to

$$T_f = \frac{\Delta l}{\alpha_l l_0} + T_0$$

$$= \frac{4.6 \times 10^{-3} \text{ m}}{\left[12.0 \times 10^{-6} \text{ (°C)}^{-1}\right](11.9 \text{ m})} + 10°C$$

$$= 32.2°C + 10°C = 42.2°C \ \ (108°F)$$

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Thermal Stresses

19.D2 *The ends of a cylindrical rod 6.4 mm (0.25 in.) in diameter and 250 mm (10 in.) long are mounted between rigid supports. The rod is stress free at room temperature [20°C (68°F)]; and upon cooling to -40°C (-40°F), a maximum thermally induced tensile stress of 125 MPa (18,125 psi) is possible. Of which of the following metals or alloys may the rod be fabricated: aluminum, copper, brass, 1025 steel, and tungsten? Why?*

Solution

This is really a materials selection problem in which we must decide for which of the five metals listed, the stress in the rod will not exceed 125 MPa (18,125 psi), when it is heated while its ends are mounted in rigid supports. Upon examination of Equation 19.8, it may be noted that all we need do is to compute the $E\alpha_l\Delta T$ product for each of the candidate materials, and then note for which of them the stress is less than the stipulated maximum. [The value of ΔT is $T_0 - T_f$ = 20°C – (–40°C) = 60°C.] These parameters and their product for each of the alloys are tabulated below. (Modulus of elasticity values were taken from Table 6.1, while the α_l values came from Table 19.1.)

Alloy	α_l (°C)$^{-1}$	E (MPa)	$\alpha_l E\Delta T$ (MPa)
Aluminum	23.6×10^{-6}	69×10^3	98
Copper	17.0×10^{-6}	110×10^3	112
Brass	20.0×10^{-6}	97×10^3	116
1025 Steel	12.0×10^{-6}	207×10^3	149
Tungsten	4.5×10^{-6}	407×10^3	110

Thus, aluminum, copper, brass, and tungsten are suitable candidates.

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19.D3 *(a) What are the units for the thermal shock resistance parameter (TSR)? (b) Rank the following ceramic materials according to their thermal shock resistance: glass-ceramic (Pyroceram), partially stabilized zirconia, and borosilicate (Pyrex) glass. Appropriate data may be found in Tables B.2, B.4, B.6, and B.7 of Appendix B.*

Solution

(a) This portion of the problem asks that we cite the units for the thermal shock resistance parameter (*TSR*). From Equation 19.9

$$TSR = \frac{\sigma_f \left(\text{N/m}^2\right) k \,(\text{W/m-K})}{E\left(\text{N/m}^2\right) \alpha_l (^\circ\text{C})^{-1}} = \text{W/m}$$

(Note: in reducing units in the above expression, we have assumed that units of temperature in K and °C are equivalent)

(b) Now we are asked to rank glass-ceramic (Pyroceram), partially-stabilized zirconia, and borosilicate (Pyrex) glass as to their thermal shock resistance. Thus, all we need do is calculate, for each, the value of *TSR* using Equation 19.9. Values of E, σ_f, α_l, and k are found, respectively, in Tables B.2, B.4, B.6, and B.7, Appendix B. (Note: whenever a range for a property value in these tables is cited, the average of the extremes is used.)

For the glass-ceramic

$$TSR = \frac{\sigma_f k}{E \alpha_l}$$

$$= \frac{(247 \text{ MPa})(3.3 \text{ W/m-K})}{\left(120 \times 10^3 \text{ MPa}\right)\left[6.5 \times 10^{-6} (^\circ\text{C})^{-1}\right]} = 1045 \text{ W/m}$$

For partially-stabilized zirconia

$$TSR = \frac{(1150 \text{ MPa})(2.7 \text{ W/m-K})}{\left(205 \times 10^3 \text{ MPa}\right)\left[9.6 \times 10^{-6} (^\circ\text{C})^{-1}\right]} = 1578 \text{ W/m}$$

And, for borosilicate glass

$$TSR = \frac{(69 \text{ MPa})(1.4 \text{ W/m-K})}{\left(70 \times 10^3 \text{ MPa}\right)\left[3.3 \times 10^{-6} (^\circ\text{C})^{-1}\right]} = 418 \text{ W/m}$$

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Thus, these materials may be ranked according to their thermal shock resistance from the greatest to the least as follows: partially-stabilized zirconia, glass-ceramic, and borosilicate glass.

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19.D4 *Equation 19.9, for the thermal shock resistance of a material, is valid for relatively low rates of heat transfer. When the rate is high, then, upon cooling of a body, the maximum temperature change allowable without thermal shock, ΔT_f, is approximately*

$$\Delta T_f = \frac{\sigma_f}{E\alpha_l}$$

where σ_f is the fracture strength. Using the data in Tables B.2, B.4, and B.6 (Appendix B), determine ΔT_f for a glass-ceramic (Pyroceram), partially stabilized zirconia, and fused silica.

Solution

We want to compute the maximum temperature change allowable without thermal shock for these three ceramic materials, which temperature change is a function of the fracture strength, elastic modulus, and linear coefficient of thermal expansion. These data and the ΔT_f's are tabulated below. (Values for E, σ_f, and α_l are taken from Tables B.2, B.4, B.6 in Appendix B.)

Material	σ_f(MPa)	E (MPa)	α_l (°C)$^{-1}$	ΔT_f(°C)
Glass ceramic	247	120×10^3	6.5×10^{-6}	317
Zirconia	1150	205×10^3	9.6×10^{-6}	584
Fused silica	104	73×10^3	0.4×10^{-6}	3562

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CHAPTER 20

MAGNETIC PROPERTIES

PROBLEM SOLUTIONS

Basic Concepts

20.1 *A coil of wire 0.20 m long and having 200 turns carries a current of 10 A.*

(a) What is the magnitude of the magnetic field strength H?

(b) Compute the flux density B if the coil is in a vacuum.

(c) Compute the flux density inside a bar of titanium that is positioned within the coil. The susceptibility for titanium is found in Table 20.2.

(d) Compute the magnitude of the magnetization M.

Solution

(a) We may calculate the magnetic field strength generated by this coil using Equation 20.1 as

$$H = \frac{NI}{l}$$

$$= \frac{(200 \text{ turns})(10 \text{ A})}{0.20 \text{ m}} = 10,000 \text{ A - turns/m}$$

(b) In a vacuum, the flux density is determined from Equation 20.3. Thus,

$$B_0 = \mu_0 H$$

$$= (1.257 \times 10^{-6} \text{ H/m})(10,000 \text{ A - turns/m}) = 1.257 \times 10^{-2} \text{ tesla}$$

(c) When a bar of titanium is positioned within the coil, we must use an expression that is a combination of Equations 20.5 and 20.6 in order to compute the flux density given the magnetic susceptibility. Inasmuch as $\chi_m = 1.81 \times 10^{-4}$ (Table 20.2), then

$$B = \mu_0 H + \mu_0 M = \mu_0 H + \mu_0 \chi_m H = \mu_0 H(1 + \chi_m)$$

$$= (1.257 \times 10^{-6} \text{ H/m})(10,000 \text{ A - turns/m})(1 + 1.81 \times 10^{-4})$$

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$$= 1.257 \times 10^{-2} \text{ tesla}$$

which is essentially the same result as part (b). This is to say that the influence of the titanium bar within the coil makes an imperceptible difference in the magnitude of the *B* field.

(d) The magnetization is computed from Equation 20.6:

$$M = \chi_m H = (1.81 \times 10^{-4})(10{,}000 \text{ A - turns/m}) = 1.81 \text{ A/m}$$

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20.2 *Demonstrate that the relative permeability and the magnetic susceptibility are related according to Equation 20.7.*

Solution

This problem asks us to show that χ_m and μ_r are related according to $\chi_m = \mu_r - 1$. We begin with Equation 20.5 and substitute for *M* using Equation 20.6. Thus,

$$B = \mu_0 H + \mu_0 M = \mu_0 H + \mu_0 \chi_m H$$

But *B* is also defined in Equation 20.2 as

$$B = \mu H$$

When the above two expressions are set equal to one another as

$$\mu H = \mu_0 H + \mu_0 \chi_m H$$

This leads to

$$\mu = \mu_0 (1 + \chi_m)$$

If we divide both sides of this expression by μ_0, and from the definition of μ_r (Equation 20.4), then

$$\frac{\mu}{\mu_0} = \mu_r = 1 + \chi_m$$

or, upon rearrangement

$$\chi_m = \mu_r - 1$$

which is the desired result.

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20.3 *It is possible to express the magnetic susceptibility χ_m in several different units. For the discussion of this chapter, χ_m was used to designate the volume susceptibility in SI units, that is, the quantity that gives the magnetization per unit volume (m^3) of material when multiplied by H. The mass susceptibility χ_m (kg) yields the magnetic moment (or magnetization) per kilogram of material when multiplied by H; and, similarly, the atomic susceptibility χ_m(a) gives the magnetization per kilogram-mole. The latter two quantities are related to χ_m through the relationships*

$\chi_m = \chi_m(kg) \times$ *mass density (in kg/m^3)*

$\chi_m(a) = \chi_m(kg) \times$ *atomic weight (in kg)]*

When using the cgs–emu system, comparable parameters exist, which may be designated by χ'_m, χ'_m(g), and χ'_m(a); the χ_m and χ'_m are related in accordance with Table 20.1. From Table 20.2, χ_m for silver is -2.38×10^{-5}; convert this value into the other five susceptibilities.

Solution

For this problem, we want to convert the volume susceptibility of copper $(\text{i.e., } -2.38 \times 10^{-5})$ into other systems of units.

For the mass susceptibility

$$\chi_m(\text{kg}) = \frac{\chi_m}{\rho\,(\text{kg/m}^3)}$$

$$= \frac{-2.38 \times 10^{-5}}{10.49 \times 10^3\ \text{kg/m}^3} = -2.27 \times 10^{-9}$$

For the atomic susceptibility

$$\chi_m(\text{a}) = \chi_m(\text{kg}) \times [\text{atomic weight (in kg)}]$$

$$= (-2.27 \times 10^{-9})(0.10787\ \text{kg/mol}) = -2.45 \times 10^{-10}$$

For the cgs-emu susceptibilities,

$$\chi'_m = \frac{\chi_m}{4\pi} = \frac{-2.38 \times 10^{-5}}{4\pi} = -1.89 \times 10^{-6}$$

$$\chi'_m(\text{g}) = \frac{\chi'_m}{\rho(\text{g/cm}^3)} = \frac{-1.89 \times 10^{-6}}{10.49\ \text{g/cm}^3} = -1.80 \times 10^{-7}$$

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$$\chi'_m(\text{a}) = \chi'_m(\text{g}) \times [\text{atomic weight (in g)}]$$

$$= (-1.80 \times 10^{-7})(107.87 \text{ g/mol}) = -1.94 \times 10^{-5}$$

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20.4 *(a) Explain the two sources of magnetic moments for electrons.*

(b) Do all electrons have a net magnetic moment? Why or why not?

(c) Do all atoms have a net magnetic moment? Why or why not?

Solution

(a) The two sources of magnetic moments for electrons are the electron's orbital motion around the nucleus, and also, its spin.

(b) Each electron will have a net magnetic moment from spin, and possibly, orbital contributions, which do not cancel for an isolated atom.

(c) All atoms do not have a net magnetic moment. If an atom has completely filled electron shells or subshells, there will be a cancellation of both orbital and spin magnetic moments.

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Diamagnetism and Paramagnetism
Ferromagnetism

20.5 *The magnetic flux density within a bar of some material is 0.435 tesla at an H field of 3.44×10^5 A/m. Compute the following for this material: (a) the magnetic permeability, and (b) the magnetic susceptibility. (c) What type(s) of magnetism would you suggest is(are) being displayed by this material? Why?*

Solution

(a) The magnetic permeability of this material may be determined according to Equation 20.2 as

$$\mu = \frac{B}{H} = \frac{0.435 \text{ tesla}}{3.44 \times 10^5 \text{ A/m}} = 1.2645 \times 10^{-6} \text{ H/m}$$

(b) The magnetic susceptibility is calculated using a combined form of Equations 20.4 and 20.7 as

$$\chi_m = \mu_r - 1 = \frac{\mu}{\mu_0} - 1$$

$$= \frac{1.2645 \times 10^{-6} \text{ H/m}}{1.257 \times 10^{-6} \text{ H/m}} - 1 = 6.0 \times 10^{-3}$$

(c) This material would display both diamagnetic and paramagnetic behavior. All materials are diamagnetic, and since χ_m is positive and on the order of 10^{-3}, there would also be a paramagnetic contribution.

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20.6 *The magnetization within a bar of some metal alloy is 3.2×10^5 A/m at an H field of 50 A/m. Compute the following: (a) the magnetic susceptibility, (b) the permeability, and (c) the magnetic flux density within this material. (d) What type(s) of magnetism would you suggest as being displayed by this material? Why?*

Solution

(a) This portion of the problem calls for us to compute the magnetic susceptibility within a bar of some metal alloy when $M = 3.2 \times 10^5$ A/m and $H = 50$ A/m. This requires that we solve for χ_m from Equation 20.6 as

$$\chi_m = \frac{M}{H} = \frac{3.2 \times 10^5 \text{ A/m}}{50 \text{ A/m}} = 6400$$

(b) In order to calculate the permeability we must employ a combined form of Equations 20.4 and 20.7 as follows:

$$\mu = \mu_r \mu_0 = (\chi_m + 1)\mu_0$$

$$= (6400 + 1)(1.257 \times 10^{-6} \text{ H/m}) = 8.05 \times 10^{-3} \text{ H/m}$$

(c) The magnetic flux density may be determined using Equation 20.2 as

$$B = \mu H = (8.05 \times 10^{-3} \text{ H/m})(50 \text{ A/m}) = 0.40 \text{ tesla}$$

(d) This metal alloy would exhibit ferromagnetic behavior on the basis of the magnitude of its χ_m (6400), which is considerably larger than the χ_m values for diamagnetic and paramagnetic materials listed in Table 20.2.

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20.7 *Compute (a) the saturation magnetization and (b) the saturation flux density for cobalt, which has a net magnetic moment per atom of 1.72 Bohr magnetons and a density of 8.90 g/cm^3.*

Solution

(a) The saturation magnetization for Co may be determined in the same manner as was done for Ni in Example Problem 20.1. Thus, using a modified form of Equation 20.9

$$M_s = 1.72 \mu_B N$$

in which μ_B is the Bohr magneton and N is the number of Co atoms per cubic meter. Also, there are 1.72 Bohr magnetons per Co atom. Now, N (the number of cobalt atoms per cubic meter) is related to the density and atomic weight of Co, and Avogadro's number according to Equation 20.10 as

$$N = \frac{\rho_{Co} N_A}{A_{Co}}$$

$$= \frac{(8.90 \times 10^6 \text{ g/m}^3)(6.022 \times 10^{23} \text{ atoms/mol})}{58.93 \text{ g/mol}}$$

$$= 9.10 \times 10^{28} \text{ atoms/m}^3$$

Therefore,

$$M_s = 1.72 \mu_B N = (1.72 \text{ BM/atom})(9.27 \times 10^{-24} \text{ A - m}^2\text{/BM})(9.10 \times 10^{28} \text{ atoms/m}^3)$$

$$= 1.45 \times 10^6 \text{ A/m}$$

(b) The saturation flux density is determined according to Equation 20.8. Thus

$$B_s = \mu_0 M_s$$

$$= (1.257 \times 10^{-6} \text{ H/m})(1.45 \times 10^6 \text{ A/m}) = 1.82 \text{ tesla}$$

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20.8 *Confirm that there are 2.2 Bohr magnetons associated with each iron atom, given that the saturation magnetization is 1.70 × 10^6 A/m, that iron has a BCC crystal structure, and that the unit cell edge length is 0.2866 nm.*

Solution

We want to confirm that there are 2.2 Bohr magnetons associated with each iron atom. Therefore, let n_B' be the number of Bohr magnetons per atom, which we will calculate. This is possible using a modified and rearranged form of Equation 20.9—that is

$$n_B' = \frac{M_s}{\mu_B N}$$

Now, N is just the number of atoms per cubic meter, which is the number of atoms per unit cell (two for BCC, Section 3.4) divided by the unit cell volume-- that is,

$$N = \frac{2}{V_C} = \frac{2}{a^3}$$

a being the BCC unit cell edge length. Thus

$$n_B' = \frac{M_s}{N\mu_B} = \frac{M_s\, a^3}{2\mu_B}$$

$$= \frac{(1.70 \times 10^6\ \text{A/m})\left[(0.2866 \times 10^{-9}\ \text{m})^3/\text{unit cell}\right]}{(2\ \text{atoms/unit cell})(9.27 \times 10^{-24}\ \text{A-m}^2/\text{BM})}$$

$$= 2.16\ \text{Bohr magnetons/atom}$$

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20.9 *Assume there exists some hypothetical metal that exhibits ferromagnetic behavior and that has (1) a simple cubic crystal structure (Figure 3.24), (2) an atomic radius of 0.153 nm, and (3) a saturation flux density of 0.76 tesla. Determine the number of Bohr magnetons per atom for this material.*

Solution

We are to determine the number of Bohr magnetons per atom for a hypothetical metal that has a simple cubic crystal structure, an atomic radius of 0.153 nm, and a saturation flux density of 0.76 tesla. It becomes necessary to employ Equation 20.8 and a modified form of Equation 20.9 as follows:

$$n_B = \frac{M_s}{\mu_B N} = \frac{\frac{B_s}{\mu_0}}{\mu_B N} = \frac{B_s}{\mu_0 \mu_B N}$$

Here n_B is the number of Bohr magnetons per atom, and N is just the number of atoms per cubic meter, which is the number of atoms per unit cell [one for simple cubic (Figure 3.23)] divided by the unit cell volume—that is,

$$N = \frac{1}{V_C}$$

which, when substituted into the above equation gives

$$n_B = \frac{B_s V_C}{\mu_0 \mu_B}$$

For the simple cubic crystal structure (Figure 3.23), $a = 2r$, where r is the atomic radius, and $V_C = a^3 = (2r)^3$. Substituting this relationship into the above equation yields

$$n_B = \frac{B_s (2r)^3}{\mu_0 \mu_B}$$

$$= \frac{(0.76 \text{ tesla})(8)\left(0.153 \times 10^{-9} \text{ m}\right)^3}{\left(1.257 \times 10^{-6} \text{ H/m}\right)\left(9.27 \times 10^{-24} \text{ A-m}^2/\text{BM}\right)} = 1.87 \text{ Bohr magnetons/atom}$$

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20.10 *There is associated with each atom in paramagnetic and ferromagnetic materials a net magnetic moment. Explain why ferromagnetic materials can be permanently magnetized whereas paramagnetic ones cannot.*

Solution

Ferromagnetic materials may be permanently magnetized (whereas paramagnetic ones may not) because of the ability of net spin magnetic moments of adjacent atoms to align with one another. This mutual magnetic moment alignment in the same direction exists within small volume regions--domains. When a magnetic field is applied, favorably oriented domains grow at the expense of unfavorably oriented ones, by the motion of domain walls. When the magnetic field is removed, there remains a net magnetization by virtue of the resistance to movement of domain walls; even after total removal of the magnetic field, the magnetization of some net domain volume will be aligned near the direction that the external field was oriented.

For paramagnetic materials, there is no magnetic dipole coupling, and, consequently, domains do not form. When a magnetic field is removed, the atomic dipoles assume random orientations, and no magnetic moment remains.

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Antiferromagnetism and Ferrimagnetism

20.11 *Consult another reference in which Hund's rule is outlined, and on its basis explain the net magnetic moments for each of the cations listed in Table 20.4.*

Solution

Hund's rule states that the spins of the electrons of a shell will add together in such a way as to yield the maximum magnetic moment. This means that as electrons fill a shell the spins of the electrons that fill the first half of the shell are all oriented in the same direction; furthermore, the spins of the electrons that fill the last half of this same shell will all be aligned and oriented in the opposite direction. For example, consider the iron ions in Table 20.4; from Table 2.2, the electron configuration for the outermost shell for the Fe atom is $3d^6 4s^2$. For the Fe^{3+} ion the outermost shell configuration is $3d^5$, which means that five of the ten possible $3d$ states are filled with electrons. According to Hund's rule the spins of all of these electrons are aligned, there will be no cancellation, and therefore, there are five Bohr magnetons associated with each Fe^{3+} ion, as noted in the table. For Fe^{2+} the configuration of the outermost shell is $3d^6$, which means that the spins of five electrons are aligned in one direction, and the spin of a single electron is aligned in the opposite direction, which cancels the magnetic moment of one of the other five; thus, this yields a net moment of four Bohr magnetons.

For Mn^{2+} the electron configuration is $3d^5$, the same as Fe^{3+}, and, therefore it will have the same number of Bohr magnetons (i.e., five).

For Co^{2+} the electron configuration is $3d^7$, which means that the spins of five electrons are in one direction, and two are in the opposite direction, which gives rise to a net moment of three Bohr magnetons.

For Ni^{2+} the electron configuration is $3d^8$ which means that the spins of five electrons are in one direction, and three are in the opposite direction, which gives rise to a net moment of two Bohr magnetons.

For Cu^{2+} the electron configuration is $3d^9$ which means that the spins of five electrons are in one direction, and four are in the opposite direction, which gives rise to a net moment of one Bohr magneton.

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20.12 *Estimate (a) the saturation magnetization, and (b) the saturation flux density of nickel ferrite [$(NiFe_2O_4)_8$], which has a unit cell edge length of 0.8337 nm.*

Solution

(a) The saturation magnetization of nickel ferrite is computed in the same manner as Example Problem 20.2; from Equation 20.13

$$M_s = \frac{n_B \mu_B}{a^3}$$

Now, n_B is just the number of Bohr magnetons per unit cell. The net magnetic moment arises from the Ni^{2+} ions, of which there are eight per unit cell, each of which has a net magnetic moment of two Bohr magnetons (Table 20.4). Thus, n_B is sixteen. Therefore, from the above equation

$$M_s = \frac{(16 \text{ BM/unit cell})(9.27 \times 10^{-24} \text{ A-m}^2/\text{BM})}{(0.8337 \times 10^{-9} \text{ m})^3/\text{unit cell}}$$

$$= 2.56 \times 10^5 \text{ A/m}$$

(b) This portion of the problem calls for us to compute the saturation flux density. From Equation 20.8

$$B_s = \mu_0 M_s$$

$$= (1.257 \times 10^{-6} \text{ H/m})(2.56 \times 10^5 \text{ A/m}) = 0.32 \text{ tesla}$$

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20.13 *The chemical formula for manganese ferrite may be written as $(MnFe_2O_4)_8$ because there are eight formula units per unit cell. If this material has a saturation magnetization of 5.6×10^5 A/m and a density of 5.00 g/cm^3, estimate the number of Bohr magnetons associated with each Mn^{2+} ion.*

Solution

We want to compute the number of Bohr magnetons per Mn^{2+} ion in $(MnFe_2O_4)_8$. Let n_B represent the number of Bohr magnetons per Mn^{2+} ion; then, using Equation 20.9, we have

$$M_s = n_B \mu_B N$$

in which N is the number of Mn^{2+} ions per cubic meter of material. But, from Equation 20.10

$$N = \frac{\rho N_A}{A}$$

Here A is the molecular weight of $MnFe_2O_4$ (230.64 g/mol). Thus, combining the previous two equations

$$M_s = \frac{n_B \mu_B \rho N_A}{A}$$

or, upon rearrangement (and expressing the density in units of grams per meter cubed),

$$n_B = \frac{M_s A}{\mu_B \rho N_A}$$

$$= \frac{(5.6 \times 10^5 \text{ A/m})(230.64 \text{ g/mol})}{(9.27 \times 10^{-24} \text{ A-m}^2/\text{BM})(5.00 \times 10^6 \text{ g/m}^3)(6.022 \times 10^{23} \text{ ions/mol})}$$

$$= 4.6 \text{ Bohr magnetons/Mn}^{2+} \text{ ion}$$

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20.14 *The formula for yttrium iron garnet ($Y_3Fe_5O_{12}$) may be written in the form $Y_3^cFe_2^aFe_3^dO_{12}$, where the superscripts a, c, and d represent different sites on which the Y^{3+} and Fe^{3+} ions are located. The spin magnetic moments for the Y^{3+} and Fe^{3+} ions positioned in the a and c sites are oriented parallel to one another and antiparallel to the Fe^{3+} ions in d sites. Compute the number of Bohr magnetons associated with each Y^{3+} ion, given the following information: (1) each unit cell consists of eight formula ($Y_3Fe_5O_{12}$) units; (2) the unit cell is cubic with an edge length of 1.2376 nm; (3) the saturation magnetization for this material is 1.0×10^4 A/m; and (4) assume that there are 5 Bohr magnetons associated with each Fe^{3+} ion.*

Solution

For this problem we are given that yttrium iron garnet may be written in the form $Y_3^cFe_2^aFe_3^dO_{12}$ where the superscripts *a*, *c*, and *d* represent different sites on which the Y^{3+} and Fe^{3+} ions are located, and that the spin magnetic moments for the ions on *a* and *c* sites are oriented parallel to one another and antiparallel to the Fe^{3+} ions on the *d* sites. We are to determine the number of Bohr magnetons associated with each Y^{3+} ion given that each unit cell consists of eight formula units, the unit cell is cubic with an edge length of 1.2376 nm, the saturation magnetization for the material is 1.0×10^4 A/m, and that there are 5 Bohr magnetons for each Fe^{3+} ion.

The first thing to do is to calculate the number of Bohr magnetons per unit cell, which we will denote n_B. Solving for n_B using Equation 20.13, we get

$$n_B = \frac{M_s a^3}{\mu_B}$$

$$= \frac{(1.0 \times 10^4 \text{ A/m})(1.2376 \times 10^{-9} \text{ m})^3}{9.27 \times 10^{-24} \text{ A - m}^2/\text{BM}} = 2.04 \text{ Bohr magnetons/unit cell}$$

Now, there are 8 formula units per unit cell or $\frac{2.04}{8} = 0.255$ Bohr magnetons per formula unit. Furthermore, for each formula unit there are two Fe^{3+} ions on *a* sites and three Fe^{3+} on *d* sites which magnetic moments are aligned antiparallel. Since there are 5 Bohr magnetons associated with each Fe^{3+} ion, the net magnetic moment contribution per formula unit from the Fe^{3+} ions is 5 Bohr magnetons. This contribution is antiparallel to the contribution from the Y^{3+} ions, and since there are three Y^{3+} ions per formula unit, then

$$\text{No. of Bohr magnetons/Y}^{3+} = \frac{0.255 \text{ BM} + 5 \text{ BM}}{3} = 1.75 \text{ BM}$$

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The Influence of Temperature on Magnetic Behavior

20.15 *Briefly explain why the magnitude of the saturation magnetization decreases with increasing temperature for ferromagnetic materials, and why ferromagnetic behavior ceases above the Curie temperature.*

Solution

For ferromagnetic materials, the saturation magnetization decreases with increasing temperature because the atomic thermal vibrational motions counteract the coupling forces between the adjacent atomic dipole moments, causing some magnetic dipole misalignment. Ferromagnetic behavior ceases above the Curie temperature because the atomic thermal vibrations are sufficiently violent so as to completely destroy the mutual spin coupling forces.

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Domains and Hysteresis

20.16 *Briefly describe the phenomenon of magnetic hysteresis, and why it occurs for ferromagnetic and ferrimagnetic materials.*

The phenomenon of magnetic hysteresis and an explanation as to why it occurs for ferromagnetic and ferrimagnetic materials is given in Section 20.7.

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20.17 *A coil of wire 0.1 m long and having 15 turns carries a current of 1.0 A.*

(a) Compute the flux density if the coil is within a vacuum.

(b) A bar of an iron–silicon alloy, the B-H behavior for which is shown in Figure 20.29, is positioned within the coil. What is the flux density within this bar?

(c) Suppose that a bar of molybdenum is now situated within the coil. What current must be used to produce the same B field in the Mo as was produced in the iron–silicon alloy [part (b)] using 1.0 A?

Solution

(a) This portion of the problem asks that we compute the flux density in a coil of wire 0.1 m long, having 15 turns, and carrying a current of 1.0 A, and that is situated in a vacuum. Combining Equations 20.1 and 20.3, and solving for B yields

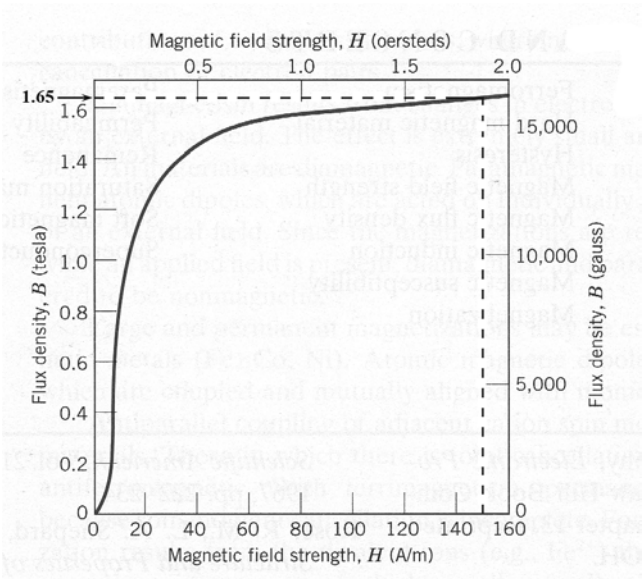
$$B_0 = \mu_0 H = \frac{\mu_0 NI}{l}$$

$$= \frac{(1.257 \times 10^{-6}\ \text{H/m})(15\ \text{turns})(1.0\ \text{A})}{0.1\ \text{m}} = 1.89 \times 10^{-4}\ \text{tesla}$$

(b) Now we are to compute the flux density with a bar of the iron-silicon alloy, the B-H behavior for which is shown in Figure 20.29. It is necessary to determine the value of H using Equation 20.1 as

$$H = \frac{NI}{l} = \frac{(15\ \text{turns})(1.0\ \text{A})}{0.1\ \text{m}} = 150\ \text{A-turns/m}$$

Using the curve in Figure 20.29, $B = 1.65$ tesla at $H = 150$ A-turns/m, as demonstrated below.



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(c) Finally, we are to assume that a bar of Mo is situated within the coil, and to calculate the current that is necessary to produce the same B field as when the iron-silicon alloy in part (b) was used. Molybdenum is a paramagnetic material having a χ_m of 1.19×10^{-4} (Table 20.2). Combining Equations 20.2, 20.4, and 20.7 we solve for H

$$H = \frac{B}{\mu} = \frac{B}{\mu_0 \mu_r} = \frac{B}{\mu_0 (1 + \chi_m)}$$

And when Mo is positioned within the coil, then, from the above equation

$$H = \frac{1.65 \text{ tesla}}{(1.257 \times 10^{-6} \text{ H/m})(1 + 1.19 \text{ x } 10^{-4})} = 1.312 \times 10^6 \text{ A - turns/m}$$

Now, the current may be determined using Equation 20.1:

$$I = \frac{Hl}{N} = \frac{(1.312 \times 10^6 \text{ A - turns/m})(0.1 \text{ m})}{15 \text{ turns}} = 8750 \text{ A}$$

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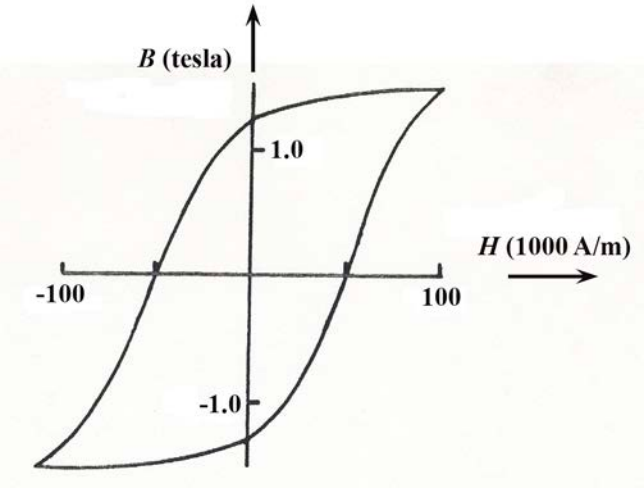
20.18 *A ferromagnetic material has a remanence of 1.25 teslas and a coercivity of 50,000 A/m. Saturation is achieved at a magnetic field intensity of 100,000 A/m, at which the flux density is 1.50 teslas. Using these data, sketch the entire hysteresis curve in the range H = –100,000 to +100,000 A/m. Be sure to scale and label both coordinate axes.*

Solution

The *B* versus *H* curve for this material is shown below.



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20.19 *The following data are for a transformer steel:*

***H* (*A/m*)**	***B* (*teslas*)**	***H* (*A/m*)**	***B* (*teslas*)**
0	*0*	*200*	*1.04*
10	*0.03*	*400*	*1.28*
20	*0.07*	*600*	*1.36*
50	*0.23*	*800*	*1.39*
100	*0.70*	*1000*	*1.41*
150	*0.92*		

(a) Construct a graph of B versus H.

(b) What are the values of the initial permeability and initial relative permeability?

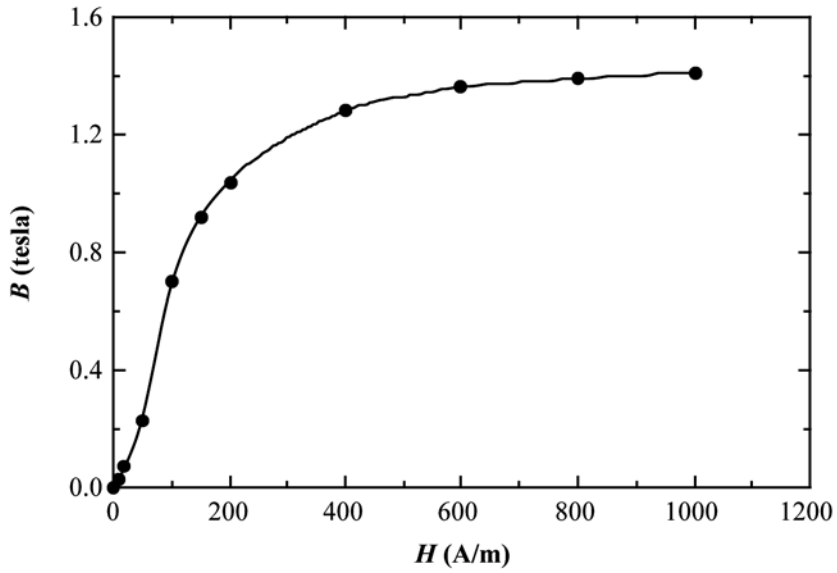
(c) What is the value of the maximum permeability?

(d) At about what H field does this maximum permeability occur?

(e) To what magnetic susceptibility does this maximum permeability correspond?

Solution

(a) The *B*-*H* data for the transformer steel provided in the problem statement are plotted below.



(b) The first four data points are plotted below.

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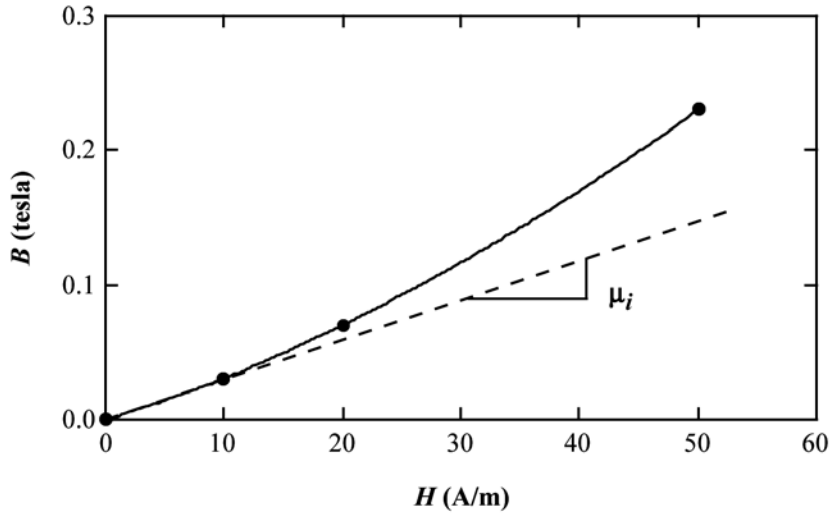


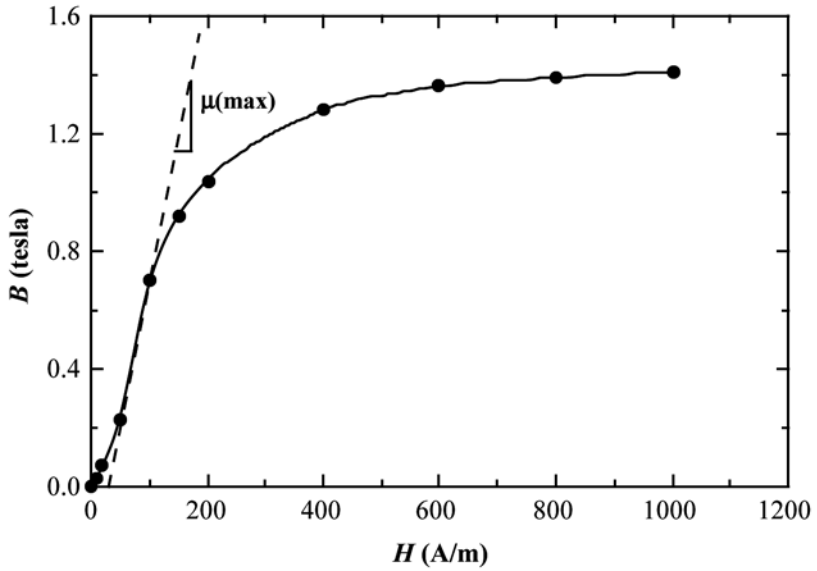
The slope of the initial portion of the curve is μ_i (as shown), is

$$\mu_i = \frac{\Delta B}{\Delta H} = \frac{(0.15 - 0)\ \text{tesla}}{(50 - 0)\ \text{A/m}} = 3.0 \times 10^{-3}\ \text{H/m}$$

Also, the initial relative permeability, μ_{ri}, (Equation 20.4) is just

$$\mu_{ri} = \frac{\mu_i}{\mu_0} = \frac{3.0 \times 10^{-3}\ \text{H/m}}{1.257 \times 10^{-6}\ \text{H/m}} = 2387$$

(c) The maximum permeability is the tangent to the *B*-*H* curve having the greatest slope; it is drawn on the plot below, and designated as μ(max).



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The value of μ(max) is (modifying Equation 20.2)

$$\mu(\text{max}) = \frac{\Delta B}{\Delta H} = \frac{(1.3 - 0.3)\ \text{tesla}}{(160 - 45)\ \text{A - m}} = 8.70 \times 10^{-3}\ \text{H/m}$$

(d) The H field at which μ(max) occurs is approximately 80 A/m [as taken from the plot shown in part (c)].

(e) We are asked for the maximum susceptibility, χ(max). Combining modified forms of Equations 20.7 and 20.4 yields

$$\chi(\text{max}) = \mu_r(\text{max}) - 1 = \frac{\mu(\text{max})}{\mu_0} - 1$$

$$= \frac{8.70 \times 10^{-3}\ \text{H/m}}{1.257 \times 10^{-6}\ \text{H/m}} - 1 = 6920$$

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20.20 *An iron bar magnet having a coercivity of 4000 A/m is to be demagnetized. If the bar is inserted within a cylindrical wire coil 0.15 m long and having 100 turns, what electric current is required to generate the necessary magnetic field?*

Solution

In order to demagnetize a magnet having a coercivity of 4000 A/m, an H field of 4000 A/m must be applied in a direction opposite to that of magnetization. According to Equation 20.1

$$I = \frac{Hl}{N}$$

$$= \frac{(4000\ \text{A/m})(0.15\ \text{m})}{100\ \text{turns}} = 6\ \text{A}$$

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20.21 *A bar of an iron–silicon alloy having the B–H behavior shown in Figure 20.29 is inserted within a coil of wire 0.20 m long and having 60 turns, through which passes a current of 0.1 A.*

(a) What is the B field within this bar?

(b) At this magnetic field,

(i) What is the permeability?

(ii) What is the relative permeability?

(iii) What is the susceptibility?

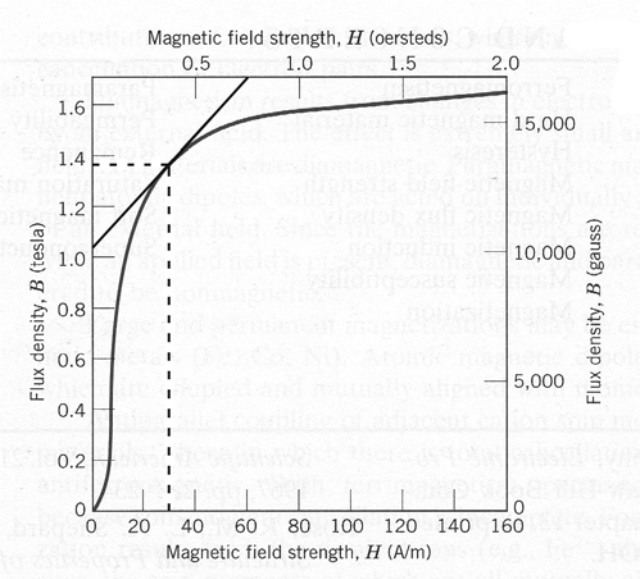
(iv) What is the magnetization?

Solution

(a) We want to determine the magnitude of the B field within an iron-silicon alloy, the B-H behavior for which is shown in Figure 20.29, when $l = 0.20$ m, $N = 60$ turns, and $I = 0.1$ A. Applying Equation 20.1

$$H = \frac{NI}{l} = \frac{(60 \text{ turns})(0.1 \text{ A})}{0.20 \text{ m}} = 30 \text{ A/m}$$

Below is shown the B-versus-H plot for this material. The B value from the curve corresponding to $H = 30$ A/m is about 1.37 tesla.



(b)

(i) The permeability at this field is just $\Delta B/\Delta H$ of the tangent of the B-H curve at $H = 30$ A/m. The slope of this line as drawn in the above figure is

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$$\mu = \frac{\Delta B}{\Delta H} = \frac{(1.70 - 1.04)\ \text{tesla}}{(60 - 0)\ \text{A/m}} = 1.10 \times 10^{-2}\ \text{H/m}$$

(ii) From Equation 20.4, the relative permeability is

$$\mu_r = \frac{\mu}{\mu_0} = \frac{1.10 \times 10^{-2}\ \text{H/m}}{1.257 \times 10^{-6}\ \text{H/m}} = 8751$$

(iii) Using Equation 20.7, the susceptibility is

$$\chi_m = \mu_r - 1 = 8751 - 1 = 8750$$

(iv) The magnetization is determined from Equation 20.6 as

$$M = \chi_m H = (8750)(30\ \text{A/m}) = 2.63 \times 10^5\ \text{A/m}$$

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Magnetic Anisotropy

20.22 *Estimate saturation values of H for single-crystal iron in [100], [110], and [111] directions.*

Solution

This problem asks for us to estimate saturation values of H for single crystal iron in the [100], [110], and [111] directions. All we need do is read values of H at the points at which saturation is achieved on the [100], [110], and [111] curves for iron shown in Figure 20.17. Saturation in the [100] direction is approximately 5400 A/m. Corresponding values in [110] and [111] directions are approximately 40,000 and 47,000 A/m, respectively.

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20.23 *The energy (per unit volume) required to magnetize a ferromagnetic material to saturation (E_s) is defined by the following equation:*

$$E_s = \int_0^{M_s} \mu_0 H \, dM$$

That is, E_s is equal to the product of μ_0 and the area under an M versus H curve, to the point of saturation referenced to the ordinate (or M) axis—for example, in Figure 20.17 the area between the vertical axis and the magnetization curve to M_s. Estimate E_s values (in J/m^3) for single-crystal nickel in [100], [110], and [111] directions.

Solution

In this problem we are asked to estimate the energy required to magnetize single crystals of nickel in [100], [110], and [111] directions. These energies correspond to the products of μ_0 and the areas between the vertical axis of Figure 20.17 and the three curves for single crystal nickel taken to the saturation magnetization. For the [100] direction this area is about 15.8×10^8 A^2/m^2. When this value is multiplied by the value of μ_0 (1.257×10^{-6} H/m), we get a value of about 1990 J/m^3. The corresponding approximate areas for [110] and [111] directions are 9.6×10^8 A^2/m^2 and 3.75×10^8 A^2/m^2, respectively; when multiplied by μ_0 the respective energies for [110] and [111] directions are 1210 and 470 J/m^3.

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Soft Magnetic Materials
Hard Magnetic Materials

20.24 *Cite the differences between hard and soft magnetic materials in terms of both hysteresis behavior and typical applications.*

Solution

Relative to hysteresis behavior, a hard magnetic material has a high remanence, a high coercivity, a high saturation flux density, high hysteresis energy losses, and a low initial permeability; a soft magnetic material, on the other hand, has a high initial permeability, a low coercivity, and low hysteresis energy losses.

With regard to applications, hard magnetic materials are utilized for permanent magnets; soft magnetic materials are used in devices that are subjected to alternating magnetic fields such as transformer cores, generators, motors, and magnetic amplifier devices.

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20.25 *Assume that the commercial iron (99.95 wt% Fe) in Table 20.5 just reaches the point of saturation when inserted within the coil in Problem 20.1. Compute the saturation magnetization.*

Solution

We want to determine the saturation magnetization of the 99.95 wt% Fe in Table 20.5, if it just reaches saturation when inserted within the coil described in Problem 20.1—i.e., $l = 0.20$ m, $N = 200$ turns, and $A = 10$ A. It is first necessary to compute the H field within this coil using Equation 20.1 as

$$H_s = \frac{NI}{l} = \frac{(200 \text{ turns})(10 \text{ A})}{0.20 \text{ m}} = 10{,}000 \text{ A - turns/m}$$

Now, the saturation magnetization may be determined from a rearranged form of Equation 20.5 as

$$M_s = \frac{B_s - \mu_0 H_s}{\mu_0}$$

The value of B_s in Table 20.5 is 2.14 tesla; thus,

$$M_s = \frac{(2.14 \text{ tesla}) - \left(1.257 \times 10^{-6} \text{ H/m}\right)\left(10{,}000 \text{ A/m}\right)}{1.257 \times 10^{-6} \text{ H/m}}$$

$$= 1.69 \times 10^6 \text{ A/m}$$

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20.26 *Figure 20.30 shows the B-versus-H curve for a steel alloy.*

(a) What is the saturation flux density?

(b) What is the saturation magnetization?

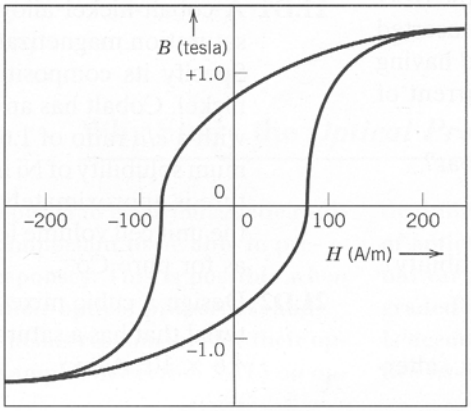
(c) What is the remanence?

(d) What is the coercivity?

(e) On the basis of data in Tables 20.5 and 20.6, would you classify this material as a soft or hard magnetic material? Why?

Solution

The *B*-versus-*H* curve of Figure 20.30 is shown below.



(a) The saturation flux density for the steel, the *B*-*H* behavior for which is shown in Figure 20.30, is 1.3 tesla, the maximum *B* value shown on the plot.

(b) The saturation magnetization is computed from Equation 20.8 as

$$M_s = \frac{B_s}{\mu_0}$$

$$= \frac{1.3 \text{ tesla}}{1.257 \times 10^{-6} \text{ H/m}} = 1.03 \times 10^6 \text{ A/m}$$

(c) The remanence, B_r, is read from this plot as from the hysteresis loop shown in Figure 20.14; its value is about 0.80 tesla.

(d) The coercivity, H_c, is read from this plot as from Figure 20.14; the value is about 80 A/m.

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(e) On the basis of Tables 20.5 and 20.6, this is most likely a soft magnetic material. The saturation flux density (1.3 tesla) lies within the range of values cited for soft materials, and the remanence (0.80 tesla) is close to the values given in Table 20.6 for hard magnetic materials. However, the H_c (80 A/m) is significantly lower than for hard magnetic materials. Also, if we estimate the area within the hysteresis curve, we get a value of approximately 250 J/m^3, which is in line with the hysteresis loss per cycle for soft magnetic materials.

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Magnetic Storage

20.27 *Briefly explain the manner in which information is stored magnetically.*

The manner in which information is stored magnetically is discussed in Section 20.11.

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Superconductivity

20.28 *For a superconducting material at a temperature T below the critical temperature T_C, the critical field H_C (T), depends on temperature according to the relationship*

$$H_C(T) = H_C(0)\left(1 - \frac{T^2}{T_C^2}\right) \qquad (20.14)$$

where $H_C(0)$ is the critical field at 0 K.

(a) Using the data in Table 20.7, calculate the critical magnetic fields for tin at 1.5 and 2.5 K..

(b) To what temperature must tin be cooled in a magnetic field of 20,000 A/m for it to be superconductive?

Solution

(a) Given Equation 20.14 and the data in Table 20.7, we are asked to calculate the critical magnetic fields for tin at 1.5 and 2.5 K. From the table, for Sn, $T_C = 3.72$ K and $B_C(0) = 0.0305$ tesla. Thus, from Equation 20.2

$$H_C(0) = \frac{B_C(0)}{\mu_0}$$

$$= \frac{0.0305 \text{ tesla}}{1.257 \times 10^{-6} \text{ H/m}} = 2.43 \times 10^4 \text{ A/m}$$

Now, solving for $H_C(1.5)$ and $H_C(2.5)$ using Equation 20.14 yields

$$H_C(T) = H_C(0)\left[1 - \frac{T^2}{T_C^2}\right]$$

$$H_C(1.5) = \left(2.43 \times 10^4 \text{ A/m}\right)\left[1 - \frac{(1.5 \text{ K})^2}{(3.72 \text{ K})^2}\right] = 2.03 \times 10^4 \text{ A/m}$$

$$H_C(2.5) = \left(2.43 \times 10^4 \text{ A/m}\right)\left[1 - \frac{(2.5 \text{ K})^2}{(3.72 \text{ K})^2}\right] = 1.33 \times 10^4 \text{ A/m}$$

(b) Now we are to determine the temperature to which tin must be cooled in a magnetic field of 20,000 A/m in order for it to be superconductive. All we need do is to solve for T from Equation 20.14—i.e.,

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$$T = T_C\sqrt{1 - \frac{H_C(T)}{H_C(0)}}$$

And, since the value of $H_C(0)$ was computed in part (a) (i.e., 24,300 A/m), then

$$T = (3.72\ \text{K})\sqrt{1 - \frac{20{,}000\ \text{A/m}}{24{,}300\ \text{A/m}}} = 1.56\ \text{K}$$

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20.29 *Using Equation 20.14, determine which of the superconducting elements in Table 20.7 are superconducting at 3 K and in a magnetic field of 15,000 A/m.*

Solution

We are asked to determine which of the superconducting elements in Table 20.7 are superconducting at 3 K and in a magnetic field of 15,000 A/m. First of all, in order to be superconductive at 3 K within any magnetic field, the critical temperature must be greater than 3 K. Thus, aluminum, titanium, and tungsten may be eliminated upon inspection. Now, for each of lead, mercury, and tin it is necessary, using Equation 20.14, to compute the value of $H_C(3)$—also substituting for $H_C(0)$ from Equation 20.3; if $H_C(3)$ is greater than 15,000 A/m then the element will be superconductive. Hence, for Pb

$$H_C(2) = H_C(0)\left[1 - \frac{T^2}{T_C^2}\right] = \frac{B_C(0)}{\mu_0}\left[1 - \frac{T^2}{T_C^2}\right]$$

$$= \frac{0.0803 \text{ tesla}}{1.257 \times 10^{-6} \text{ H/m}}\left[1 - \frac{(3.0 \text{ K})^2}{(7.19 \text{ K})^2}\right] = 5.28 \times 10^4 \text{ A/m}$$

Since this value is greater than 15,000 A/m, Pb will be superconductive.

Similarly for Hg

$$H_C(3) = \frac{0.0411 \text{ tesla}}{1.257 \times 10^{-6} \text{ H/m}}\left[1 - \frac{(3.0 \text{ K})^2}{(4.15 \text{ K})^2}\right] = 1.56 \times 10^4 \text{ A/m}$$

Inasmuch as this value is greater than 15,000 A/m, Hg will be superconductive.

As for Sn

$$H_C(3) = \frac{0.0305 \text{ tesla}}{1.257 \times 10^{-6} \text{ H/m}}\left[1 - \frac{(3.0 \text{ K})^2}{(3.72 \text{ K})^2}\right] = 8.48 \times 10^3 \text{ A/m}$$

Therefore, Sn is not superconductive.

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20.30 *Cite the differences between type I and type II superconductors.*

Solution

For type I superconductors, with increasing magnetic field the material is completely diamagnetic and superconductive below H_C, while at H_C conduction becomes normal and complete magnetic flux penetration takes place. On the other hand, for type II superconductors upon increasing the magnitude of the magnetic field, the transition from the superconducting to normal conducting states is gradual between lower-critical and upper-critical fields; so also is magnetic flux penetration gradual. Furthermore, type II generally have higher critical temperatures and critical magnetic fields.

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20.31 *Briefly describe the Meissner effect.*

Solution

The Meissner effect is a phenomenon found in superconductors wherein, in the superconducting state, the material is diamagnetic and completely excludes any external magnetic field from its interior. In the normal conducting state complete magnetic flux penetration of the material occurs.

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20.32 *Cite the primary limitation of the new superconducting materials that have relatively high critical temperatures.*

Solution

The primary limitation of the new superconducting materials that have relatively high critical temperatures is that, being ceramics, they are inherently brittle.

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DESIGN PROBLEMS

Ferromagnetism

20.D1 *A cobalt–nickel alloy is desired that has a saturation magnetization of 1.3 × 10^6 A/m. Specify its composition in weight percent nickel. Cobalt has an HCP crystal structure with c/a ratio of 1.623, whereas the maximum solubility of Ni in Co at room temperature is approximately 35 wt%. Assume that the unit cell volume for this alloy is the same as for pure Co.*

Solution

For this problem we are asked to determine the composition of a Co-Ni alloy that will yield a saturation magnetization of 1.3 × 10^6 A/m. To begin, let us compute the number of Bohr magnetons per unit cell n_B for this alloy from an expression that results from combining Equations 20.11 and 20.12. That is

$$n_B = N' V_C = \frac{M_s V_C}{\mu_B}$$

in which M_s is the saturation magnetization, V_C is the unit cell volume, and μ_B is the magnitude of the Bohr magneton. According to Equation 3.S1 (the solution to Problem 3.7), for HCP

$$V_C = 6R^2 c\sqrt{3}$$

And, as stipulated in the problem statement, $c = 1.623a$; in addition, for HCP, the unit cell edge length, a, and the atomic radius, R are related as $a = 2R$. Making these substitutions into the above equation leads to the following:

$$V_C = 6R^2 c\sqrt{3} = 6R^2 (1.623a)\sqrt{3} = 6R^2 (1.623)(2R)\sqrt{3}$$

$$= 12R^3 (1.623)\sqrt{3}$$

From the inside of the front cover of the book, the value of R for Co is given as 0.125 nm (1.25 × 10^{-10} m). Therefore,

$$V_C = (12)(1.25 \times 10^{-10}\ \text{m})^3 (1.623)\sqrt{3}$$

$$= 6.59 \times 10^{-29}\ \text{m}^3$$

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And, now solving for n_B from the first equation above, yields

$$n_B = = \frac{M_s V_C}{\mu_B} = \frac{(1.3 \times 10^6 \text{ A/m})(6.59 \times 10^{-29} \text{ m}^3/\text{unit cell})}{\frac{9.27 \times 10^{-24} \text{ A-m}^2}{\text{Bohr magneton}}}$$

$$= 9.24 \frac{\text{Bohr magneton}}{\text{unit cell}}$$

Inasmuch as there are 1.72 and 0.60 Bohr magnetons for each of Co and Ni (Section 20.4), and, for HCP, there are 6 equivalent atoms per unit cell (Section 3.4), if we represent the fraction of Ni atoms by x, then

$$n_B = 9.24 \text{ Bohr magnetons/unit cell}$$

$$= \left(\frac{0.60 \text{ Bohr magnetons}}{\text{Ni atom}}\right)\left(\frac{6x \text{ Ni atoms}}{\text{unit cell}}\right) + \left(\frac{1.72 \text{ Bohr magnetons}}{\text{Co atom}}\right)\left[\frac{(6)(1 - x) \text{ Co atoms}}{\text{unit cell}}\right]$$

And solving for x, the fraction of Ni atoms , $x = 0.161$, or 16.1 at% Ni.

In order to convert this composition to weight percent, we employ Equation 4.7 as

$$C_{Ni} = \frac{C'_{Ni} A_{Ni}}{C'_{Ni} A_{Ni} + C'_{Co} A_{Co}} \times 100$$

$$= \frac{(16.1 \text{ at\%})(58.69 \text{ g/mol})}{(16.1 \text{ at\%})(58.69 \text{ g/mol}) + (83.9 \text{ at\%})(58.93 \text{ g/mol})} \times 100$$

$$= 16.0 \text{ wt\%}$$

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Ferrimagnetism

20.D2 *Design a cubic mixed-ferrite magnetic material that has a saturation magnetization of 4.6 × 10^5 A/m.*

Solution

This problem asks that we design a cubic mixed-ferrite magnetic material that has a saturation magnetization of 4.6 × 10^5 A/m. From Example Problem 20.2 the saturation magnetization for Fe_3O_4 is 5.0 × 10^5 A/m. In order to decrease the magnitude of M_s it is necessary to replace some fraction of the Fe^{2+} with another divalent metal ion that has a smaller magnetic moment. From Table 20.4 it may be noted that Co^{2+}, Ni^{2+}, and Cu^{2+}, with 3, 2, and 1 Bohr magnetons per ion, respectively, have fewer than the 4 Bohr magnetons/Fe^{2+} ion. Let us first consider Co^{2+} (with 3 Bohr magnetons per ion) and employ Equation 20.13 to compute the number of Bohr magnetons per unit cell (n_B), assuming that the Co^{2+} addition does not change the unit cell edge length (0.839 nm, Example Problem 20.2). Thus,

$$n_B = \frac{M_s a^3}{\mu_B}$$

$$= \frac{(4.6 \times 10^5 \text{ A/m})(0.839 \times 10^{-9} \text{ m})^3/\text{unit cell}}{9.27 \times 10^{-24} \text{ A - m}^2/\text{Bohr magneton}}$$

$$= 29.31 \text{ Bohr magnetons/unit cell}$$

If we let x_{Co} represent the fraction of Co^{2+} that have substituted for Fe^{2+}, then the remaining unsubstituted Fe^{2+} fraction is equal to $1 - x_{Co}$. Furthermore, inasmuch as there are 8 divalent ions per unit cell, we may write the following expression:

$$n_B(\text{Co}) = 8\left[3x_{Co} + 4(1 - x_{Co})\right] = 29.31$$

which leads to $x_{Co} = 0.336$. Thus, if 33.6 at% of the Fe^{2+} in Fe_3O_4 are replaced with Co^{2+}, the saturation magnetization will be decreased to 4.6 × 10^5 A/m.

For the cases of Ni^{2+} and Cu^{2+} substituting for Fe^{2+}, the equivalents of the preceding equation for the number of Bohr magnetons per unit cell will read as follows:

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$$n_B(\text{Ni}) = 8\left[2x_{\text{Ni}} + 4(1 - x_{\text{Ni}})\right] = 29.31$$

$$n_B(\text{Cu}) = 8\left[x_{\text{Cu}} + 4(1 - x_{\text{Cu}})\right] = 29.31$$

with the results that

$x_{\text{Ni}} = 0.168$ (or 16.8 at%)

$x_{\text{Cu}} = 0.112$ (11.2 at%)

will yield the 4.6×10^5 A/m saturation magnetization.

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CHAPTER 21

OPTICAL PROPERTIES

Electromagnetic Radiation

21.1 *Visible light having a wavelength of 6×10^{-7} m appears orange. Compute the frequency and energy of a photon of this light.*

Solution

In order to compute the frequency of a photon of orange light, we must use Equation 21.2 as

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m/s}}{6 \times 10^{-7} \text{ m}} = 5 \times 10^{14} \text{ s}^{-1}$$

Now, for the energy computation, we employ Equation 21.3 as follows:

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J-s})(3 \times 10^8 \text{ m/s})}{6 \times 10^{-7} \text{ m}}$$

$$= 3.31 \times 10^{-19} \text{ J} \quad (2.07 \text{ eV})$$

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Light Interactions with Solids

21.2 *Distinguish between materials that are opaque, translucent, and transparent in terms of their appearance and light transmittance.*

Solution

Opaque materials are impervious to light transmission; it is not possible to see through them.

Light is transmitted diffusely through translucent materials (there is some internal light scattering). Objects are not clearly distinguishable when viewed through a translucent material.

Virtually all of the incident light is transmitted through transparent materials, and one can see clearly through them.

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Atomic and Electronic Interactions

21.3 *(a) Briefly describe the phenomenon of electronic polarization by electromagnetic radiation. (b) What are two consequences of electronic polarization in transparent materials?*

Solution

(a) The phenomenon of electronic polarization by electromagnetic radiation is described in Section 21.4.

(b) Two consequences of electronic polarization in transparent materials are absorption and refraction.

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Optical Properties of Metals

21.4 *Briefly explain why metals are opaque to electromagnetic radiation having photon energies within the visible region of the spectrum.*

Solution

The electron band structures of metals are such that empty and available electron states are adjacent to filled states. Electron excitations from filled to empty states are possible with the absorption of electromagnetic radiation having frequencies within the visible spectrum, according to Equation 21.6. The light energy is totally absorbed or reflected, and, since none is transmitted, the material is opaque.

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Refraction

21.5 *In ionic materials, how does the size of the component ions affect the extent of electronic polarization?*

Solution

In ionic materials, the larger the size of the component ions the greater the degree of electronic polarization.

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21.6 *Can a material have an index of refraction less than unity? Why or why not?*

Solution

In order for a material to have an index of refraction less than unity, the velocity of light in the material (v) would necessarily have to be greater than the velocity of light in a vacuum (Equation 21.7). This is not possible.

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21.7 *Compute the velocity of light in calcium fluoride (CaF_2), which has a dielectric constant $\in_r$ of 2.056 (at frequencies within the visible range) and a magnetic susceptibility of -1.43×10^{-5}.*

Solution

We want to compute the velocity of light in calcium fluoride given that $\varepsilon_r = 2.056$ and $\chi_m = -1.43 \times 10^{-5}$. The velocity is determined using Equation 21.8; but first, we must calculate the values of ε and μ for calcium fluoride. According to Equation 18.27

$$\varepsilon = \varepsilon_r \varepsilon_0 = (2.056)(8.85 \times 10^{-12}\ \text{F/m}) = 1.82 \times 10^{-11}\ \text{F/m}$$

Now, combining Equations 20.4 and 20.7

$$\mu = \mu_0 \mu_r = \mu_0(\chi_m + 1)$$

$$= (1.257 \times 10^{-6}\ \text{H/m})(1 - 1.43 \times 10^{-5}) = 1.257 \times 10^{-6}\ \text{H/m}$$

And, finally, from Equation 21.8

$$v = \frac{1}{\sqrt{\varepsilon\mu}}$$

$$= \frac{1}{\sqrt{(1.82 \times 10^{-11}\ \text{F/m})(1.257 \times 10^{-6}\ \text{H/m})}}$$

$$= 2.09 \times 10^{8}\ \text{m/s}$$

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21.8 *The indices of refraction of fused silica and a soda–lime glass within the visible spectrum are 1.458 and 1.51, respectively. For each of these materials determine the fraction of the relative dielectric constant at 60 Hz that is due to electronic polarization, using the data of Table 18.5. Neglect any orientation polarization effects.*

Solution

The frequencies of visible radiation are on the order of 10^{15} Hz (Figure 21.2). At these frequencies only electronic polarization is operable (Figure 18.34). Thus, ε_r from Equation 21.10 is the electronic contribution to ε_r; let us designate it as ε_r'. Or, in other words

$$\varepsilon_r' = n^2$$

For fused silica

$$\varepsilon_r'(\text{silica}) = (1.458)^2 = 2.13$$

And, for soda-lime glass

$$\varepsilon_r'(\text{glass}) = (1.51)^2 = 2.28$$

The fraction of the electronic contribution is just the ratio of ε_r' and ε_r, where ε_r values are taken from Table 18.5 (4.0 and 6.9 for fused silica and soda-lime glass, respectively). Thus

$$\frac{\varepsilon_r'(\text{silica})}{\varepsilon_r(60\ \text{Hz})} = \frac{2.13}{4.0} = 0.53$$

and

$$\frac{\varepsilon_r'(\text{glass})}{\varepsilon_r(60\ \text{Hz})} = \frac{2.28}{6.9} = 0.33$$

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21.9 *Using the data in Table 21.1, estimate the dielectric constants for borosilicate glass, periclase (MgO), poly(methyl methacrylate), and polypropylene, and compare these values with those cited in the table below. Briefly explain any discrepancies.*

Material	*Dielectric Constant (1 MHz)*
Borosilicate glass	*4.65*
Periclase	*9.65*
Poly(methyl methacrylate)	*2.76*
Polypropylene	*2.30*

Solution

This problem asks for us, using data in Table 21.1, to estimate the dielectric constants for borosilicate glass, periclase (MgO), poly(methyl methacrylate), and polypropylene, and then to compare these values with those cited in the table provided, and briefly explain any discrepancies. From Equation 21.10

$$\varepsilon_r = n^2$$

Thus, for borosilicate glass, since $n = 1.47$

$$\varepsilon_r = (1.47)^2 = 2.16$$

Similarly, for periclase

$$\varepsilon_r = (1.74)^2 = 3.03$$

And, for PMMA

$$\varepsilon_r = (1.49)^2 = 2.22$$

For polypropylene

$$\varepsilon_r = (1.49)^2 = 2.22$$

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When we compare the values of ε_r for the polymers with those in the table at frequencies of 1 MHz, there is reasonable agreement (i.e., 2.22 versus 2.76 for PMMA, and 2.22 versus 2.30 for polypropylene). However, for borosilicate glass and periclase there are some significant discrepancies (i.e., 2.16 versus 4.65 for the borosilicate glass, and 3.03 versus 9.65 for the periclase). The reason for these discrepancies is that for these two materials an ionic component to the dielectric constant is present at 1 MHz, but is absent at frequencies within the visible electromagnetic spectrum, which frequencies are on the order 10^9 MHz (10^{15} Hz). These effects may be noted in Figure 18.34.

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21.10 *Briefly describe the phenomenon of dispersion in a transparent medium.*

Solution

Dispersion in a transparent medium is the phenomenon wherein the index of refraction varies slightly with the wavelength of the electromagnetic radiation.

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Reflection

21.11 *It is desired that the reflectivity of light at normal incidence to the surface of a transparent medium be less than 6.0%. Which of the following materials in Table 21.1 are likely candidates: silica glass, Pyrex glass, corundum, spinel, polystyrene, and polytetrafluoroethylene? Justify your selection(s).*

Solution

For this problem we want to compute the maximum value of n_s in Equation 21.13 that will give $R = 0.060$. Then we are to consult Table 21.1 in order to ascertain which of the materials listed have indices of refraction less than this maximum value. From Equation 21.13

$$0.060 = \frac{(n_s - 1)^2}{(n_s + 1)^2} = \frac{n_s^2 - 2n_s + 1}{n_s^2 + 2n_s + 1}$$

or, upon rearrangement

$$0.94\, n_s^2 - 2.12\, n_s + 0.94 = 0$$

The value of n_s is determined by using the quadratic equation solution as follows:

$$n_s = \frac{-(-2.12) \pm \sqrt{(-2.12)^2 - (4)(0.94)(0.94)}}{(2)(0.94)}$$

$$= \frac{2.12 \pm 0.98}{1.88}$$

The two solutions are: $n_s(+) = 1.65$ and $n_s(-) = 0.606$. The $n_s(+)$ solution is the one that is physically reasonable. Thus, of the materials listed, silica glass, Pyrex glass, polystyrene, and PTFE have indices of refraction less than 1.65, and would be suitable for this application.

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21.12 *Briefly explain how reflection losses of transparent materials are minimized by thin surface coatings.*

Solution

The thickness and dielectric constant of a thin surface coating are selected such that there is destructive interference between the light beam that is reflected from the lens-coating interface and the light beam that is reflected from the coating-air interface; thus, the net intensity of the total reflected beam is very low.

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21.13 *The index of refraction of corundum (Al_2O_3) is anisotropic. Suppose that visible light is passing from one grain to another of different crystallographic orientation and at normal incidence to the grain boundary. Calculate the reflectivity at the boundary if the indices of refraction for the two grains are 1.757 and 1.779 in the direction of light propagation.*

Solution

This problem calls for a calculation of the reflectivity between two corundum grains having different orientations and indices of refraction (1.757 and 1.779) in the direction of light propagation, when the light is at normal incidence to the grain boundary. We must employ Equation 21.12 since the beam is normal to the grain boundary. Thus,

$$R = \left(\frac{n_2 - n_1}{n_2 + n_1} \right)^2$$

$$= \left(\frac{1.779 - 1.757}{1.779 + 1.757} \right)^2 = 3.87 \times 10^{-5}$$

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Absorption

21.14 *Zinc telluride has a band gap of 2.26 eV. Over what range of wavelengths of visible light is it transparent?*

Solution

This problem asks us to determine the range of visible light wavelengths over which ZnTe (E_g = 2.26 eV) is transparent. Only photons having energies of 2.26 eV or greater are absorbed by valence-band-to-conduction-band electron transitions. Thus, photons having energies less than 2.26 eV are not absorbed; the minimum photon energy for visible light is 1.8 eV (Equation 21.16b), which corresponds to a wavelength of 0.7 μm. From Equation 21.3, the wavelength of a photon having an energy of 2.26 eV (i.e., the band-gap energy) is just

$$\lambda = \frac{hc}{E} = \frac{(4.13 \times 10^{-15}\ \text{eV-s})(3 \times 10^{8}\ \text{m/s})}{2.26\ \text{eV}}$$

$$= 5.5 \times 10^{-7}\ \text{m} = 0.55\ \mu\text{m}$$

Thus, pure ZnTe is transparent to visible light having wavelengths between 0.55 and 0.7 μm.

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21.15 *Briefly explain why the magnitude of the absorption coefficient (β in Equation 21.18) depends on the radiation wavelength.*

Solution

The magnitude of the absorption coefficient (β in Equation 21.18) depends on the radiation wavelength for intrinsic insulators and semiconducting materials. This is because, for photons having energies less than the band-gap energy (or in terms of wavelength, when $\lambda > \frac{h c}{E_g}$), photon absorption due to valence-band-to-conduction-band electron transitions are not possible, and, therefore, the value of β will be relatively small. On the other hand, when photons having energies equal to or greater than the band gap energy (i.e., when $\lambda \leq \frac{h c}{E_g}$) these electron transitions by the absorption of photons will occur with the result that the magnitude of β will be relatively large.

In addition, there may be impurity levels that lie within the band gap (Section 21.7) from or to which electron excitations may occur with the absorption of light radiation at specific wavelengths.

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21.16 *The fraction of nonreflected radiation that is transmitted through a 10-mm thickness of a transparent material is 0.90. If the thickness is increased to 20 mm, what fraction of light will be transmitted?*

Solution

In this problem we are asked to calculate the fraction of nonreflected light transmitted through a 20-mm thickness of transparent material, given that the fraction transmitted through a 10-mm thickness is 0.90. From Equation 21.18, the fraction of nonreflected light transmitted is just I_T'/I_0'. Using this expression we must first determine the value of β**;** this is possible by algebraic manipulation of Equation 21.18. Dividing both sides of the equation by I_0', and then taking natural logarithms leads to

$$\ln\left(\frac{I_T'}{I_0'}\right) = -\beta x$$

Now solving for β and also incorporating values for I_T'/I_0' and x provided in the problem statement gives

$$\beta = -\frac{1}{x}\ln\left(\frac{I_T'}{I_0'}\right)$$

$$= -\left(\frac{1}{10\text{ mm}}\right)\ln(0.90) = 1.05 \times 10^{-2}\text{ mm}^{-1}$$

And computation of I_T'/I_0' when x = 20 mm (Equation 21.18) is as follows:

$$\frac{I_T'}{I_0'} = \exp(-\beta x)$$

$$= \exp\left[-(1.05 \times 10^{-2}\text{ mm}^{-1})(20\text{ mm})\right] = 0.81$$

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Transmission

21.17 *Derive Equation 21.19, starting from other expressions given in the chapter.*

Solution

The problem asks that we derive Equation 21.19, which is

$$I_T = I_0(1 - R)^2 \, e^{-\beta l}$$

If we examine Figure 21.7, at the front (or left) interface, some of the incident beam having intensity I_0 is reflected. Since $I_R = I_0 R$ at this surface, then

$$I_T' = I_0 - I_0 R = I_0(1 - R)$$

in which I_T' is the intensity of the nonreflected beam at the front surface that is transmitted.

Now there will be absorption of this transmitted beam as it passes through the solid and transparent medium according to Equation 21.18. Just inside the back (or right) interface, the beam has passed through a thickness l of this material ($x = l$) and, therefore, the intensity of the transmitted beam at this point (I_T'') is just

$$I_T'' = I_0(1 - R)e^{-\beta l}$$

Finally, a second reflection will occur at the back interface as the beam passes out of the medium. The intensity of the reflected beam (I_R'') is just

$$I_R'' = I_T'' R = I_0 R(1 - R)e^{-\beta l}$$

And the intensity of the final transmitted beam (I_T) becomes

$$I_T = I_T'' - I_R''$$

$$= I_0(1 - R)e^{-\beta l} - I_0 R(1 - R)e^{-\beta l}$$

$$= I_0(1 - R)^2 e^{-\beta l}$$

which is Equation 21.19, the desired expression.

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21.18 *The transmissivity T of a transparent material 20 mm thick to normally incident light is 0.85. If the index of refraction of this material is 1.6, compute the thickness of material that will yield a transmissivity of 0.75. All reflection losses should be considered.*

Solution

We are asked to compute the thickness of material to yield a transmissivity of 0.75 given that T is 0.85 when l = 20 mm, n = 1.6, and for normally incident radiation. The first requirement is that we calculate the value of β for this material using Equations 21.13 and 21.19. The value of R is determined using Equation 21.13 as

$$R = \frac{(n_s - 1)^2}{(n_s + 1)^2}$$

$$= \frac{(1.6 - 1)^2}{(1.6 + 1)^2} = 5.33 \times 10^{-2}$$

Now, it is necessary to compute the value of β using Equation 21.19. Dividing both sides of Equation 21.19 by $I_0(1 - R)^2$ leads to

$$\frac{I_T}{I_0(1 - R)^2} = e^{-\beta l}$$

And taking the natural logarithms of both sides of this expression gives

$$\ln\left[\frac{I_T}{I_0(1 - R)^2}\right] = -\beta l$$

and solving for β we get

$$\beta = -\frac{1}{l} \ln\left[\frac{I_T}{I_0(1 - R)^2}\right]$$

Since the transmissivity is T is equal to I_T/I_0, then the above equation takes the form

$$\beta = -\frac{1}{l} \ln\left[\frac{T}{(1 - R)^2}\right]$$

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Using values for l and T provided in the problem statement, as well as the value of R determined above, we solve for β as

$$\beta = -\left(\frac{1}{20\ \text{mm}}\right)\ln\left[\frac{0.85}{\left(1 - 5.33 \times 10^{-2}\right)^2}\right] = 2.65 \times 10^{-3}\ \text{mm}^{-1}$$

Now, solving for l when $T = 0.75$ using the rearranged form of Equation 21.19 above

$$l = -\frac{1}{\beta}\ln\left[\frac{T}{(1 - R)^2}\right]$$

$$= -\frac{1}{2.65 \times 10^{-3}\ \text{mm}^{-1}}\ln\left[\frac{0.75}{\left(1 - 5.33 \times 10^{-2}\right)^2}\right]$$

$$= 67.3\ \text{mm}$$

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Color

21.19 *Briefly explain what determines the characteristic color of (a) a metal and (b) a transparent nonmetal.*

Solution

(a) The characteristic color of a metal is determined by the distribution of wavelengths of the nonabsorbed light radiation that is reflected.

(b) The characteristic color of a transparent nonmetal is determined by the distribution of wavelengths of the nonabsorbed light radiation that is transmitted through the material.

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21.20 *Briefly explain why some transparent materials appear colored while others are colorless.*

Solution

For a transparent material that appears colorless, any absorption within its interior is the same for all visible wavelengths. On the other hand, if there is any selective absorption of visible light (usually by electron excitations), the material will appear colored, its color being dependent on the frequency distribution of the transmitted light beam.

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Opacity and Translucency in Insulators

21.21 *Briefly describe the three absorption mechanisms in nonmetallic materials.*

The three absorption mechanisms in nonmetallic materials involve electronic polarization, electron transitions, and scattering. Electronic polarization is described in Section 21.4; absorption by electron transitions is discussed in Sections 21.4 and 21.7; and scattering is discussed in Section 21.10.

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21.22 *Briefly explain why amorphous polymers are transparent, while predominantly crystalline polymers appear opaque or, at best, translucent.*

Solution

Amorphous polymers are normally transparent because there is no scattering of a light beam within the material. However, for semicrystalline polymers, visible light will be scattered at boundaries between amorphous and crystalline regions since they have different indices of refraction. This leads to translucency or, for extensive scattering, opacity, except for semicrystalline polymers having very small crystallites.

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Luminescence

Photoconductivity

Lasers

21.23 *(a) In your own words describe briefly the phenomenon of luminescence.*

(b) What is the distinction between fluorescence and phosphorescence?

Solution

(a) The phenomenon of luminescence is described in Section 21.11.

(b) The feature that distinguishes fluorescence from phosphorescence is the magnitude of the time interval between photon absorption and reemission events. Fluorescence is for delay times less than a second; phosphorescence occurs for longer times.

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21.24 *In your own words, briefly describe the phenomenon of photoconductivity.*

The phenomenon of photoconductivity is explained in Section 21.12.

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21.25 *Briefly explain the operation of a photographic lightmeter.*

Solution

A photographic light meter is used to measure the intensity of incident light radiation. Each photon of incident light induces a valence-band-to-conduction band electron transition in which both electrons and holes are produced, as depicted in Figure 21.5*a*. The magnitude of the photoinduced current resulting from these transitions is registered, which is proportional to the numbers of electrons and holes, and thus, the number of incident photons, or, equivalently, the intensity of the incident light radiation.

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21.26 *In your own words, describe how a ruby laser operates.*

Section 21.13 contains a description of the operation of a ruby laser.

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21.27 *Compute the difference in energy between metastable and ground electron states for the ruby laser.*

Solution

This problem asks for the difference in energy between metastable and ground electron states for a ruby laser. The wavelength of the radiation emitted by an electron transition from the metastable to ground state is cited as 0.6943 μm. The difference in energy between these states, ΔE, may be determined from a combined form of Equations 21.6 and 21.2, as

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

$$= \frac{(4.13 \times 10^{-15}\ \text{eV-s})(3 \times 10^{8}\ \text{m/s})}{6.943 \times 10^{-7}\ \text{m}}$$

$$= 1.78\ \text{eV}$$

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Optical Fibers in Communications

21.28 *At the end of Section 21.14 it was noted that the intensity of light absorbed while passing through a 16-kilometer length of optical fiber glass is equivalent to the light intensity absorbed through for a 25-mm thickness of ordinary window glass. Calculate the absorption coefficient β of the optical fiber glass if the value of β for the window glass is* $5 \times 10^{-4}\ mm^{-1}$.

Solution

This problem asks for us to determine the value of the absorption coefficient for optical fiber glass given that β for window glass is $5 \times 10^{-4}\ mm^{-1}$; furthermore, the intensity of nonabsorbed light transmitted through a 25-mm thickness of window glass is equivalent to the nonabsorbed light transmitted through a 16-km length of the optical fiber material. Using Equation 21.18, it is first necessary to compute the fraction of light transmitted through the window glass—i.e., $\frac{I_T'}{I_0'}$. Thus

$$\frac{I_T'}{I_0'} = e^{-\beta x}$$

$$= e^{-(5 \times 10^{-4}\ mm^{-1})(25\ mm)} = 0.9876$$

Now, solving for β from Equation 21.18 leads to

$$\beta = -\frac{1}{x} \ln\left(\frac{I_T'}{I_0'}\right)$$

And substitution into this expression the above value for $\frac{I_T'}{I_0'}$ (0.9876) as well as parameters for the optical fiber glass—x = 16 km = 16×10^3 m = 16×10^6 mm—yields

$$\beta = -\frac{1}{16 \times 10^6\ mm} \ln (0.9876) = 7.80 \times 10^{-10}\ mm^{-1}$$

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DESIGN PROBLEM

Atomic and Electronic Interactions

21.D1 *Gallium arsenide (GaAs) and gallium phosphide (GaP) are compound semiconductors that have room-temperature band gap energies of 1.42 and 2.25 eV, respectively, and form solid solutions in all proportions. Furthermore, the band gap of the alloy increases approximately linearly with GaP additions (in mol%). Alloys of these two materials are used for light-emitting diodes wherein light is generated by conduction band-to-valence band electron transitions. Determine the composition of a GaAs–GaP alloy that will emit orange light having a wavelength of 0.60 μm.*

Solution

This problem stipulates that GaAs and GaP have room-temperature band gap energies of 1.42 and 2.25 eV, respectively, that they form solid solutions in all proportions, that alloys of these two semiconductors are used for light-emitting diodes wherein light is generated by conduction band-to-valence band electron transitions, and that the band gap of a GaAs-GaP alloy increases approximately linearly with GaP additions (in mol%). We are asked to determine the composition of an alloy that will emit red light having a wavelength of 0.60 μm. It first becomes necessary to compute the band-gap energy corresponding to this wavelength of light using Equation 21.3 as

$$E_g = \frac{hc}{\lambda}$$

$$= \frac{(4.13 \times 10^{-15}\ \text{eV-s})(3 \times 10^{8}\ \text{m/s})}{0.60 \times 10^{-6}\ \text{m}} = 2.065\ \text{eV}$$

Realizing that at 0 mol% GaP, E_g = 1.42 eV, while at 100 mol% GaP, E_g = 2.25 eV, it is possible to set up the relationship

$$\frac{100\ \text{mol\%} - C_{\text{GaP}}}{100\ \text{mol\%} - 0\ \text{mol\%}} = \frac{2.25\ \text{eV} - 2.065\ \text{eV}}{2.25\ \text{eV} - 1.42\ \text{eV}}$$

Solving for C_{GaP}, the composition of GaP, we get C_{GaP} = 77.7 mol%.

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